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IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

IPCG Newsletter September, 2002

Conference announcement
Gordon Conference on Polymer Colloids
Tilton, New Hampshire, June 29 - July 4, 2003

Application forms and further information will be sent to all IPCG members. You can also check the Gordon Conference website:
http://www.grc.uri.edu

or contact the Conference Chair, Bob Gilbert:
gilbert@chem.usyd.edu.au

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Institute for Polymer Materials "POLYMAT" and Grupo de Ingeniería Química, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, E-20080 San Sebastián, Spain.

Reported by José M. Asua

July 2002

Recently published articles:

UTILIZATION OF NEURAL NETWORKS AS SOFT SENSORS TO MONITOR EMULSION POLYMERIZATION REACTIONS (AVERAGE PARTICLE DIAMETER AND CONVERSION)

P.H.H. Araújo, C. Sayer, J.C. de la Cal, J.M. Asua, E.L. Lima, J.C. Pinto

Latin American Applied Research, **31**, 525 (2001). (Abstract in the previous IPCGN).

FEEDBACK CONTROL OF COMPOSITION AND MWD OF NONLINEAR EMULSION COPOLYMERS

M. Vicente, J.R. Leiza, J.M. Asua

in "Polymer Colloids. Science and Technology of Latex Systems". E.S. Daniels, E.D. Sudol and M.S. El-Aasser, Editors, ACS Symp. Ser. **801**,113 (2002). (Abstract in the previous IPCGN).

IMPROVING LATEX PERFORMANCE BY USING POLYMERIZABLE SURFACTANTS

E. Aramendia, M.J. Barandiaran, J.C. de la Cal, J. Grade, T. Blease, J.M. Asua

in "Polymer Colloids. Science and Technology of Latex Systems". E.S. Daniels, E.D. Sudol and M.S. El-Aasser, Editors, ACS Symp. Ser. **801**, 168 (2002). (Abstract in the previous IPCGN).

POST-POLYMERIZATION OF VINYL ACETATE CONTAINING LATEXES

P. Ilundain, L. da Cunha, R. Salazar, D. Alvarez, M. J. Barandiaran, J. M. Asua

J. Appl. Polym. Sci., **83**(4), 923 (2002). (Abstract in the previous IPCGN).

DYNAMIC OPTIMIZATION OF NON-LINEAR EMULSION COPOLYMERIZATION SYSTEMS: OPEN-LOOP CONTROL OF COMPOSITION AND MOLECULAR WEIGHT DISTRIBUTIONS

M. Vicente, J.R. Leiza, J.M. Asua.

Chem. Eng. J., **85**, 339 (2002). (Abstract in the previous IPCGN).

CONTROL OF MICROSTRUCTURAL PROPERTIES IN EMULSION POLYMERIZATION SYSTEMS

M. Vicente, J.R. Leiza, J.M. Asua.

Macromol. Symp., **182**, 291 (2002). (Abstract in the previous IPCGN).

MINIEMULSION POLYMERIZATION

J.M. Asua

Progress in Polym. Sci. **27** (7), 1283 (2002). (Abstract in the previous IPCGN).

MODELING OF OLEFIN GAS-PHASE POLYMERIZATION IN THE MULTIZONE CIRCULATING REACTOR

J.L. Santos, M. Vecino, E. Ochoteco, M. Montes, J.M. Asua, J.C. de la Cal

DECHEMA Monographien **137**, 155 (2001).

A mathematical model for the gas-phase polymerization of olefins in a MultiZone Circulating Reactor (MZCR) is presented. The system is modeled as a series of two interconnected polymerization zones working with different gas phase compositions. The model takes into account particle and reactor levels, as well as the particle population balance. Simulations show that a wide range of product characteristics can be achieved by varying the operation conditions in the reactor.

NECESSARY EVIL NON-MIGRATORY SURFACTANT OVERCOMES DRAWBACKS OF CONVENTIONAL PRODUCTS

E. Aramendia, M.J. Barandiaran, J.M. Asua, J. Grade, T. Blease

Modern Paint and Coatings, **91**(11), 36 (2001).

The use of conventional surfactants to make aqueous polymer dispersions by emulsion polymerisation causes problems in the final adhesive and coating film due to non-uniform distribution of surfactant. The surfactant increases moisture sensitivity, affects adhesion and appearance of the dry film. This article describes a new non-migratory surfactant (NMS) technology for use in emulsion polymerisation processes. The latex and the final coating no longer show drawbacks associated with conventional surfactants.

Use of NMS technology offers advantages to the latex and to the dry film in the final application: superior colloidal stability of the latex and formulated system, superior protective properties and durability of the dry film and improved appearance

NMS technology enables an upgrade of waterborne binder properties in protective coating, paper coating and adhesive applications.

MODELING PARTICLE SIZE DISTRIBUTION (PSD) IN EMULSION COPOLYMERIZATION REACTIONS IN A CONTINUOUS LOOP REACTOR

P.H.H. Araújo, J.C. de la Cal, J.M. Asua, J.C. Pinto

Macromol. Theory Simul. **10** (8), 769 (2001).

A detailed dynamic mathematical model that describes the evolution of particle size distributions (PSDs) during emulsion copolymerization reactions in a continuous loop reactor was developed and compared with experimental data. The model is based on the assumption that two distinct particle populations exist: precursor particles and stable latex particles. Precursor particles are colloidally unstable and therefore may undergo coagulation with other precursors and be absorbed by stable latex particles. It is shown that the kinetic model is able to reproduce the rather complex dynamic behavior of the vinyl acetate/Veova10 emulsion copolymerization in a continuous loop reactor, including the development of oscillatory responses of PSDs during reaction start-up. It is also shown that, for the studied polymerization system, oscillatory responses are obtained only when both particle populations are assumed to exist and when both coagulative and micellar particle nucleations are simultaneously considered.

CHALLENGES IN ON-LINE CONTROL OF COMPOSITION AND MOLECULAR WEIGHT DISTRIBUTION OF NON-LINEAR EMULSION COPOLYMERS" IN "POLYMER COLLOIDS. SCIENCE AND TECHNOLOGY OF LATEX SYSTEMS

M. Vicente, J.R. Leiza, J.M. Asua

E.S. Daniels, E.D. Sudol and M.S. El-Aasser, Editors, ACS Symp. Ser. **801**, 113 (2002).

The applicability of the control strategies developed for the simultaneous control of copolymer composition and MWD of linear polymers to nonlinear polymer is investigated. It was shown that a reasonable control of both properties could be achieved for the emulsion copolymerization of methyl methacrylated and butyl acrylate when the process was carried out under semi-flooded conditions. The industrial implications of this process are discussed.

POLYMERIZATION OF HIGH-SOLIDS CONTENT ACRYLIC LATEXES USING NONIONIC POLYMERIZABLE SURFACTANT

E. Aramendia, M.J. Barandiaran, J. Grade, T. Blease, J.M. Asua

J. Polym. Sci. Part A: Polym. Chem., **40** (10), 1552 (2002).

Stable high solids content methyl methacrylate/butyl acrylate latexes with small particle size (in the range of 150-180 nm) were obtained by using a non-ionic polymerizable surfactant (surfmer). 3% of surfmer with respect to monomer was proven to be enough for the stabilization of the latexes. The influence of different operational variables on the stabilization of the final latex was analyzed and the conditions needed to obtain coagulum-free latex assessed. It was observed that the inorganic potassium persulfate/sodium metabisulfite initiator system provided better stability than the organic tert-butyl hydroperoxide/ascorbic acid, due to the presence of end groups. In addition, it was found that the feeding of acrylic acid during the second half of the polymerization improved the stability of the final latex. The reduction of the feeding time was found to be effective in the stabilization. Proof of the surfmer incorporation into the particles is presented.

PROCESOS DE POLIMERIZACIÓN: LA ETAPA CLAVE EN EL DESARROLLO DE POLÍMEROS CON MEJORES PRESTACIONES

J.M. Asua

Química e Industria, **1**, 13 (2002).

Polymers are the materials that present the fastest growth rate in the last half a century. Polymers are product-by-process materials whose final properties are largely determined in the polymerization process. The wide variety of polymerization processes allows the imaginative polymer scientists and engineers to produce high performance polymeric materials that meet a large range of market needs. In this article some important polymerization processes are reviewed.

EMULSION POLYMERIZATION OF STYRENE USING POYSTYRENE-B-POLY(ETHYLENE OXIDE) MACROMONOMERS AS STABILIZERS

S. Gibanel, V. Heroguez, J. Forcada

J. Polym. Sci., Part A: Polym. Chem. **40** (16), 2819 (2002).

New diblock macromonomers were used as reactive emulsifiers in the emulsion polymerization of styrene. The nature of the reactive group, the molecular weight, the length of the poly(ethylene oxide) (PEO) block, and the molecular structure of the macromonomer were systematically investigated during this process by analyzing the evolution of the conversion and particle diameters.

DISPERSION POLYMERIZATION OF STYRENE IN ETHANOL-WATER MIXTURE USING POLYSTYRENE-B-POLY(ETHYLENE OXIDE) MACROMONOMERS AS STABILIZERS

S. Gibanel, V. Heroguez, J. Forcada, Y. Gnanou

Macromolecules **35**, 2467-2473 (2002).

The dispersion polymerization of styrene in an ethanol-water mixture using polystyrene-*b*-poly(ethylene oxide) macromonomers as stabilizers has been investigated. The influence of parameters such as the nature of the polymerizable group, the hydrophilic/hydrophobic balance, the overall molar mass, and the molecular architecture of the macromonomers on the colloidal dispersion has indeed been studied. Macromonomers of rather low molar mass and exhibiting high critical micellar concentration were best suited to produce stable particles. Latex particles of rather narrow size distribution could be obtained in the range of 300-350 nm with styrenyl or maleate ended PS-*b*-PEO macromonomers.

REACTIVE SURFACTANTS IN HETEROPHASE POLYMERIZATION: COLLOIDAL PROPERTIES, FILM WATER ABSORPTION AND SURFACTANT EXUDATION

J.I. Amalvy, M.J. Unzue, H.A.S. Schoonbrood, J.M. Asua

J. Polym. Sci., Part A: Polym. Chem.**40** (17), 2994 (2002).

In this paper results obtained with latexes prepared by emulsion polymerization using a conventional surfactant and a polymerizable surfactant (surfmer) are presented. For this study well-defined styrene-butyl acrylate latexes with a conventional non-reactive surfactant (sodium dodecyl sulfate) and a maleate diester surfmer, of which films can be easily cast, were used. The latex with the surfmer was prepared following a surfmer addition strategy to maximize the amount of surfmer bound to the particle surface, and not buried in the particle interior. The latex properties in terms of mechanical stability, film water absorption and film surfactant exudation have been assessed and compared. The mechanical stability and water absorption properties of the latex prepared with surfmer were better than those of the latex with sodium dodecyl sulfate. Additionally, by using a surfmer the surfactant migration to the film-substrate and film-air interfaces can be inhibited.

REACTIVE SURFACTANTS IN HETEROPHASE POLYMERIZATION: XVII INFLUENCE OF THE SURFACTANT ON THE MECHANICAL PROPERTIES AND HYDRATION OF THE FILMS

C. Gauthier, O. Sindt, G. Vigier, A. Guyot, H.A.S. Schoonbrood, M.J. Unzue, J.M. Asua

J. Appl. Polym. Sci. **84** (9), 1686 (2002).

In the context of a European Union-supported network on "Reactive Surfactants for Heterophase Polymerization," different polymerizable surfactants (surfmers) have been synthesized and engaged in the emulsion polymerization of styrene, butyl acrylate, and acrylic acid. The thermomechanical properties of films cast from these different latices are reported in this article. The evolution of the mechanical properties with temperature and the effect of water molecules on these properties are studied. We observed that the studied surfactants do not influence the properties of the dry films. However, some differences due to grafting of reactive surfactants appeared when the films were wet. The amount of water uptake is drastically decreased when only reactive surfactants are present in the film. Concerning the mechanical behavior of the wet films, a decrease of the plastic flow stress is observed for all the samples whatever the nature of the surfactant (reactive or conventional). Hence, calorimetric measurements and dynamic mechanical analysis are used to identify the possible mechanisms that induce the change in the mechanical behavior of the latex films. In the case of reactive surfactant grafted to the polymer, the very low value of water uptake is accompanied by a plasticization of the polymer. In contrast, no plasticizing effect is observed in the case of nonreactive surfactant, even if the amount of water is very large. Finally, the tensile behavior of the styrene-butyl acrylate copolymer versus temperature is analyzed in the frame of the quasi point defects (qpd) model. Both rubber elasticity and chain orientation effects are taken into account to describe the behavior laws at large extensions (i.e., $\varepsilon \approx 1.2$).

Coming Articles

MAXIMIZING PRODUCTION AND POLYMER QUALITY (MWD AND COMPOSITION) IN EMULSION POLYMERIZATION REACTORS WITH LIMITED CAPACITY HEAT REMOVAL

M. Vicente, J.R. Leiza, J.M. Asua.

Chem. Eng. Sci. (accepted). (Abstract in the previous IPCGN).

SEEDED SEMIBATCH EMULSION POLYMERIZATION OF N-BA: EFFECT OF THE SEED PROPERTIES

C. Plessis, G. Arzamendi, M. Agnely, J.R. Leiza, J.M. Asua

J. Polym. Sci. Part A: Polym. Chem. (accepted). (Abstract in the previous IPCGN).

COPOLYMERS

J.R. Leiza, J.M. Asua

Kirk-Othmer Encyclopedia of Chemical Technology. On-line Edition. John Wiley & sons, New York (accepted).

The preparation, properties, use and characterization of synthetic copolymers is reviewed and the future trends discussed. The different copolymer structures are detailed and the nomenclature explained. The copolymerization reactions (free radical including controlled free radical, anionic, cationic, ring-opening, catalytic and step-growth) are discussed emphasizing the copolymer structures attainable through each polymerization mechanism. Industrially important random, alternating, block, graft, star and hyperbranched copolymers are discussed in terms of the processes used to produce them and the properties achieved. Their main uses and trade names are also detailed. Future trends are discussed.

CONTROL OF THE ADHESIVE PROPERTIES OF N-BUTYL ACRYLATE/STYRENE LATEXES

O. Elizalde, M. Vicente, J.R. Leiza, J.M. Asua.

Polym. React. Eng. (accepted).

A model relating the adhesive properties and the complete molecular weight distribution of n-butyl acrylate/styrene latexes of fixed copolymer molar composition (85/15) was constructed using partial least squares regression (PLS-R). This quantitative relationship allows the prediction of the adhesive properties of the latexes from MWD measurements. After validation of the model, it was combined with a control strategy, which allows the production of latexes of controlled copolymer composition and MWD. The resulting system can be regarded as a method for the control of the adhesive properties of the latex. This methodology was satisfactorily validated experimentally by the production of two latexes of different adhesive performance.

Submitted articles

MOLECULAR WEIGHTS IN EMULSION COPOLYMERIZATION OF BUTYL ACRYLATE/STYRENE (50/50)

N. Zoco, L. López de Arbina, J.R. Leiza, J.M. Asua, G. Arzamendi

J. Polym. Sci. Part A: Polym. Chem.

A model relating the adhesive properties and the complete molecular weight distribution of n-butyl acrylate/styrene latexes of fixed copolymer molar composition (85/15) was constructed using partial least squares regression (PLS-R). This quantitative relationship allows the prediction of the adhesive properties of the latexes from MWD measurements. After validation of the model, it was combined with a control strategy, which allows the production of latexes of controlled copolymer composition and MWD. The resulting system can be regarded as a method for the control of the adhesive properties of the latex. This methodology was satisfactorily validated experimentally by the production of two latexes of different adhesive performance.

KNOWLEDGE BASED CHOICE OF THE INITIATOR TYPE FOR MONOMER REMOVAL BY POST-POLYMERIZATION

P. Ilundain, D. Alvarez, L. da Cunha, R. Salazar, M.J. Barandiaran, J.M. Asua

J. Polym. Sci. Part A: Polym. Chem.

The mechanisms involved in the monomer removal by post-polymerization were investigated with the aim of establishing a criterion to select the most effective initiator systems. Three redox systems yielding radicals of different hydrophobicity were studied. It was found that efficiency in monomer removal by post-polymerization increased with the hydrophobicity of the radical formed from the initiator system. This result was independent of the water-solubility of the residual monomer. The mechanistic reasons for this result are discussed.

DEVELOPMENT OF PARTICLE MORPHOLOGY IN EMULSION POLYMERIZATION. 4.- EFFECT OF THE RADICAL CONCENTRATION PROFILE

S. Mendoza-Fernández, L.J. González-Ortiz, J.M. Asua

Macromolecules

A mathematical model for the dynamic development of the particle morphology in emulsion polymerization is presented. The model is able to account for the radical concentration profiles arising from the surface anchoring effect, which allows to study the effect of the initiator type on particle morphology.

MODEL REDUCTION IN EMULSION POLYMERIZATION USING HYBRID FIRST PRINCIPLES/ARTIFICIAL NEURAL NETWORKS MODELS

A. d´Anjou, F J. Torrealdea, J.R. Leiza, J.M. Asua, G. Arzamendi

A first-principles mathematical model for emulsion polymerization was reduced by using a hybrid mathematical model composed by artificial neural networks (ANN) and material balances. The goal was to have an accurate model that may be integrated fast enough to be used for on-line optimization purposes. In the reduced model the polymerization rate and the instantaneous weight-average molecular weight were calculated by means of artificial neural networks. These ANNs were incorporated to first principles material balances. The accuracy of the reduced model under a wide range of conditions was assessed. Savings in computer time were achieved by using the reduced model, which makes it suitable for on-line optimization purposes.

Contribution from the Department of Polymerization Reactions
Polymer Institute,Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republic

Reported by **Jaroslav Barton**
(August 15, 2002)

Microemulsion polymerization of styrene in the presence of macroinimer**.**

U. Yildiz (Kocaeli University, Department of Chemistry, 41300, Kocaeli, Turkey) and I. Capek (Polymer Institute, Slovak Academy of Sciences, 842 36, Bratislava, Slovak Republic).

Abstract

The o/w electrosterically- and sterically-stabilized microemulsion polymerization of styrene with and without macromonomeric azoinitiator (MIM) have been investigated. The microemulsion polymerization stabilized by the ionic emulsifier (SDS) and the nonionic emulsifier Tween 20 was initiated by ammonium peroxodisulfate (APS)/sodium thiosulfate (STS) redox system at low temperature. A typical macroinimer (MIM) was synthesized by the reaction of 4,4'-dicyano-4,4'-azovaleryl chloride (ACPC), polyethylene glycol (PEG) and 4-vinylbenzyl chloride as described in ref. [1]. The molecular weight, M_n, of the MIM determined by GPC as $1.5 \cdot 10^3$ g/mole.

Polymerization Procedure

Batch microemulsion polymerization of styrene (St) was carried out at 25°C with the recipe comprising 7.5 g St, 15 g SDS (or Tween 20, Tw20), 75 g water, 0.2372 g STS and 0.3424 g APS. The amount of MIM was taken as 2 and 10% of monomer, that is, 0.15 and 0.75 g.

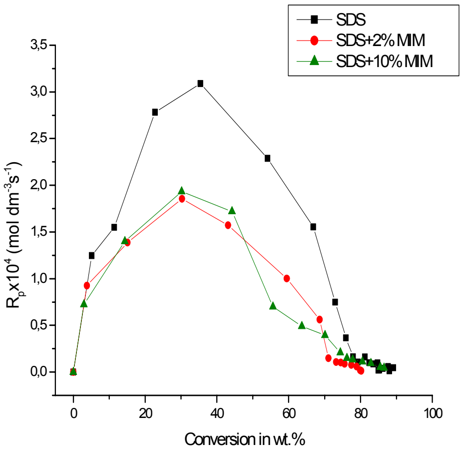
Results and Discussion

The final conversion of the sterically stabilized microemulsion (at 5 h) was observed to slightly very with the MIM concentration: 80 %/without MIM, 96%/10 wt.% MIN, and 92%/2 wt.% MIM. The final conversion in the SDS-stablized microemulsion was much below 90% conversion under the same reaction conditions.

Variations of the rate of polymerization (R_p) with conversion and MIM concentration are illustrated in Fig. 1. The three rate intervals (with a distinct Interval 2) typical for the emulsion polymerization do not appear. On the contrary, the profiles of non-stationary rate intervals, typical for the microemulsion polymerization, appear [2].

First the rate of polymerization (R_p) abruptly increases to the maximum ($R_{p,max}$) and then abruptly decreases with conversion. In all three systems, the $R_{p,max}$ is located at ca. 30-35% conversion range.

Fig. 1. *Variation of the polymerization rate he microemulsion polymerization of styrene initiated by APS and STS in the presence of MIM (in SDS media) with the monomer conversion*



The addition of MIM decreases the rate of polymerization and the decrease in R_p is nearly independent of MIM concentration. The continuous particle nucleation initiates the deviation of the present system from the classical emulsion polymerization. The two-nonstationary rate intervals are generally discussed in terms of two pposite effects; 1) the continuous increase of particle number and 2) decrease of monomer concentration at the reaction loci with conversion [3,4]. Table 1 and Fig. 1 show that the sterically (Tw 20)-stabilized microemulsion is by one order, at least, in magnitude faster than the electrostatically (SDS)- stabilized microemulsion.

The start of polymerization is accompanied by the formation of relatively large particles (ca. 300–400 nm in diameter) in the systems with SDS alone and SDS + 2 wt.% MIM. The growth of polymer particles most probably is attributed to flocculation of unstable particles between themselves or to flocculation of unstable particles with particle size up to ca. 50 % conversion could result from both the continuous particle nucleation and the shrinking of highly monomer-swollen polymer particles. The light-scattering measurements show that the large highly-monomer swollen polymer particles were not detected at medium conversion. They are supposed to serve as a monomer reservoir at medium conversion.The different colloidal parameters of St/SDS microemulsion at 25 and 70 ^{o}C probably results from the different behavior of SDS at low and high temperatures. The degree of micelle ionization increases while the aggregation number of SDS decrease with increasing temperature [5]. The formation of large initial particles is also observed in the SDS/10 wt.% MIM system. The presence of larger amount of MIM (10 wt.%), however, strongly depresses the size of polymer particles formed after the start of polymerization. This can be attributed to the co-emulsifier activity of PEO-derived MIM. Furthermore, the addition of MIM (2 or 10 wt.%) decreases the size of polymer particles at medium as well as at high conversion and the decrease is more pronounced in the run with 10 wt.% MIM. In all three systems the average particle size decreases with conversion and reaches the plateau beyond ca. 30 % conversion.

Table 1 *Variation of kinetic and colloidal parameter with time and MIM concentration in the microemulsion polymerization of styrene.*

Time (min.)	R_p x 10^4 (mol dm^{-3} s^{-1})		
	Tw 20	Tw 20/ 2% MIM	Tw 20/ 10% MIM
0			
2	38,643	49,711	42,339
5	2,027	3,654	4,78
10	1,113		
15		0,138	0,211
20	0,211		
25		0,078	0,148
35		0,03	0,099
40	0,074		
55		0,062	0,111
60	0,078		
75		0,045	0,189
90	0,038		
120	0,028	0,034	0,0448
150	0,029	0,039	0,0265
180	0,003	0,005	0,005
210	0,001	0,002	0,004
270	0	0,001	0
300	0	0	0

The very fast polymerization with Tw 20 did not allow to obtain the particle size data above ca. 40-50% conversion. The particle size was also decreased above ca. 40-50% conversion. It is interesting to note that the number of polymer particles is larger in the sterically-stabilized microemulsion than in the electrostatically- stabilized microemulsion. The higher stabilizing efficiency of nonionic emulsifier Tw 20 in the comparison to that of ionic emulsifier SDS probably results from the opposite effect of temperature on both emulsifiers. SDS emulsifier seems to be a good stabilizer at high temperature while Tw 20 at low temperature.

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Acknowledgements *This project was supported by TÜBITAK. One of authors appreciates the support by VEGA through the grant number 2/1014/21.*

Work in progress :

* Water phase titration studies of Winsor IV (w/o) inverse microemulsions.

* Transformation of acrylamide containing Winsor IV (w/o) inverse microemulsion to Winsor II (w/o), Winsor I (o/w) and Winsor IV (o/w) microemulsions and polymerization of acrylamide in separated microemulsion phases.

POLYMER COLLOID GROUP NEWSLETTER

Contribution from Institut Charles Sadron (CRM)
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reported by **Françoise CANDAU**

Synthesis in inverse emulsion and associating behavior of hydrophobically modified polyacrylamides

(M. Pabon, J-M. Corpart, J. Selb, F. Candau)

In the past decade, extensive studies in academic and industrial laboratories have focused on the development of water-soluble associating polymers for their use as thickeners in many fields of applications, for example in fracturing and drilling fluids, in latex paint technology, coatings or cosmetics. Their thickening properties in aqueous solution are due to the association of a few hydrophobic units carried out by a hydrophilic backbone.

Hydrophobically modified polyacrylamides form an important class of associating polymers. They are usually obtained by polymerization in solution or by a micellar polymerization technique in which the hydrophobe is solubilized into micelles dispersed in an aqueous medium (F. Candau, J. Selb, *Adv. Colloid Interface Sci.* 1999, 79, 149). However, a drawback of both processes is the low solid content in the final material (a few weight percent).

Recently, we have extended the classical inverse emulsion polymerization technique to the synthesis of hydrophobically modified water-soluble polymers (HMWSPs). Two different routes were investigated:

- In the first one, the hydrophilic backbone of the copolymers was formed from an acrylamide / sodium acrylate mixture. The incorporation of the hydrophobic groups (< 0.5 mol%) was achieved by free-radical copolymerization of these water-soluble monomers with a series of amphiphilic comonomers, the isooctylphenoxy-poly(oxyethylene)(*n*) methacrylates, whose number of EO units was varied from 1 to 12.

- In the second case, acrylamide was copolymerized with a conventional hydrophobic comonomer, namely *N,N*-dihexylacrylamide or *N,N*-diphenylacrylamide instead of the amphiphilic comonomers previously investigated. The choice of the last comonomers was dictated by the fact that the use of *N,N*-dialkylacrylamides instead of *N*-monoalkylacrylamides leads to copolymers homogeneous in composition and with a more efficient thickening ability (E Volpert, J. Selb, F. Candau, *Macromolecules* 1996, 29, 1452).

In both cases, the products of the reaction were hydrophobically modified water-soluble polymers of high molecular weight encapsulated within water droplets dispersed in an organic medium. Kinetic studies showed that the full-conversion samples were rather homogeneous in composition because of the specificity of the process. A mechanistic scheme has been proposed to account for the incorporation level of the comonomer as a function of its hydrophile-lipophile balance and the nature of the redox initiator (hydrophilic or lipophilic).

The rheological properties of the HMWSPs in aqueous solutions were investigated as a function of the comonomer content and the nature of the initiator with steady-flow experiments. The thickening properties were directly correlated to the conditions of synthesis and were optimal when the initiator and the comonomer were located in two distinct phases. An examination of the viscosity as a function of the shear rate and time showed that these solutions had all the characteristics of associating polymers. The complex rheological behavior was the result of the balance between interchain and intrachain hydrophobic liaisons and the kinetics of disorganization and reorganization of the network structure.

RECENT PUBLICATIONS

1. *Synthesis in inverse emulsion and properties of water-soluble associating polymers.*
M. Pabon, J-M. Corpart, J. Selb, F. Candau.
J. Appl. Polym. Sci. 84, 1418-1430 (2002)
http://dx.doi.org/10.1002/app.10337

2. Microphase separation in weakly charged hydrophobic polyelectrolytes
O. Braun, F. Boué , F. Candau
Eur. Phys. J. E 7, 141-151 (2002)
http://dx.doi.org/10.1140/epje/i200101149

3. *Polymerization in nanostructured media: applications to the synthesis of associative polymers.*
F. Candau, O. Braun, F. Essler, K. Stähler, J. Selb.
Macromol. Symp. 179, 13-26 (2002)

4. Contrôle de la structure et des propriétés de polymères hydrosolubles associatifs synthétisés par copolymérisation micellaire. (Control of the structure and properties of water-soluble associating polymers synthesized by micellar copolymerization)
M.R. Caputo, J. Selb.
Entropie 235/236, 108-117 (2001)

5. *Fluorocarbon-Hydrocarbon Nonionic Surfactants Mixtures: A Study of their Miscibility.*
P. Barthélémy, V. Tomao, J. Selb, Y. Chaudier, B. Pucci.
Langmuir 18, 2557-2563 (2002)
http://dx.doi.org/10.1021/la011600u

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1- Work in progress

B. Charleux

Characterization of aqueous micellar solutions of amphiphilic block copolymers of poly(acrylic acid) and polystyrene prepared via ATRP. Toward the control of the number of particles in emulsion polymerization.

C. Burguière, C. Chassenieux and B. Charleux (*submitted*)

A series of diblock, triblock and star-block copolymers composed of polystyrene and poly(acrylic acid) were synthesized by ATRP. The structure of the copolymers, the size of the blocks and the composition were varied, keeping however a short polystyrene block and a polyacrylic acid content larger than 60 mol% to allow solubility in alkaline water. Their micellization was studied by static and dynamic light scattering and the influence of their structural characteristics on the aggregation number, N_{agg}, was examined at low salt concentration and alkaline pH. It was shown that micelles were in a thermodynamic equilibrium state and that N_{agg} followed the power law $N_{agg} \sim N_A^{-0.9}.N_S^2$ (with N_A, the total number of acrylic acid units in the copolymer and N_S, the total number of styrene units), that is characteristic of amphiphile micelles formed from strongly segregated block copolymers. Moreover, N_{agg} was independent of salt concentration in the investigated range. The same copolymers were previously used as stabilizers in emulsion polymerization [Burguière et al. Macromolecules 2001, 34, 4439]. The final latex particle concentration, N_p, was compared with N_m, the initial micelle concentration. This enabled us to conclude that among the block copolymers studied, those with high acid content behaved like low molar mass surfactants. In contrast, those with low acid content formed micelles that could be directly nucleated to create latex particles, allowing a good control over N_p.

Controlled free-radical polymerization: a way to design polymer architecture and surface properties of latex particles.

C. Farcet, C. Burguière and B. Charleux (submitted)

This review article aims at presenting various aspects of controlled free-radical polymerization in conjunction with aqueous dispersed systems. In a first part, nitroxide-mediated controlled free-radical polymerization performed in emulsion and miniemulsion systems is exposed, from both kinetic and synthetic viewpoints. In a second part, the use of amphiphilic block copolymers as stabilizers in emulsion polymerization is described as a tool to control the number of particles and their surface properties. Finally, aqueous polymerization initiated from the surface of latex particles is reported.

Kinetic Study of Nitroxide-Mediated Controlled Free-Radical Polymerization of n-Butyl Acrylate in Aqueous Miniemulsion.

C. Farcet, J. Nicolas, B. Charleux (submitted)

Controlled free-radical homopolymerization of n-butyl acrylate was studied in aqueous miniemulsion at 112 and 125 °C, using a low molar mass alkoxyamine unimolecular initiator and an acyclic beta-phosphonylated nitroxide mediator, the N-*tert*-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, also called SG1. Polymerizations led to stable latexes with 20 wt% solids and were obtained with neither coagulation during synthesis nor destabilization over time. However, in contrast to latexes obtained via classical free-radical polymerization, average particle size of the final latexes was large, with broad particle size distribution. The initial $[SG1]_0/[alkoxyamine]_0$ molar ratio was shown to control the rate of polymerization. The fraction of SG1 released upon macroradical self-termination was small with respect to alkoxyamine initial concentration, indicating a very low fraction of dead chains. Average molar masses were controlled by the initial concentration of alkoxyamine and increased linearly with monomer conversion. Molar mass distribution was narrow, depending on the initial concentration of free nitroxide in the system. The initiator efficiency was lower than 1 at 112 °C but was very significantly improved when either a macroinitiator was used at 112 °C, or the polymerization temperature was raised to 125 °C.

F. Ganachaud

Unpublished work

Polycondensation in miniemulsion : synthesis of polyester latexes by diester/diol condensation

I. Kunsunga, C. Bui, F. Ganachaud

The extensive work done in the team on cyclosiloxane ionic polymerization in miniemulsion showed that high molar mass polymer chains were generated mainly through polycondensation of silanol terminated chains. In order to extend this concept to other monomers, we started a general study on polycondensation in miniemulsion. The polycondensation of diacids and diols have been mainly described by Saam and coll. in various patents and articles using a cationic surfactant, namely dodecylbenzene sulfonic acid (DBSA). We extended this work using diesters and diols (easier miniemulsion preparation) and using more hydrophobic surfactants. Hydrolysis reaction of polyester chains is quite slow but far from negligible. The only chance to generate polymers rather than oligomers (of 5-6 units) consists in increasing the rate of polycondensation, principally by adding a suitable catalyst soluble in the organic phase, where the polycondensation proceeds. This is under way.

Colloidal Improvements in the Cationic Polymerization of p-Methoxystyrene in Miniemulsion

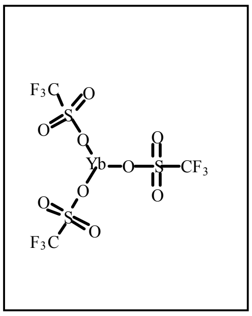
R. Dos Santos Costa, S. Cauvin, F. Ganachaud (manuscript under preparation)

We showed before that pMOS could be polymerized in the presence of DBSA to generate polymer chains of about 1200 g/mol with a nice polydispersity. Some additives were selected to improve the particle size, the colloidal stability and the rate of (interfacial) polymerization. Using a bialkyl acid surfactant increases its ability to stay at the interface and favors faster initiation rate and less termination by water. For comparable particle size compared to DBSA systems, the rate is increased by a factor of 5. The addition of an hydrophobe such as hexadecane greatly decreased the average particle size of the miniemulsion (90 nm in place of 200 nm) and thus favors faster polymerization rate. In addition, the fast coalescence observed previously while the monomer was totally consumed did not appear here. Combining both additives should give rise to fast and stable pMOS latex particles.

Cationic Polymerization of p-Methoxystyrene in Miniemulsion in the Presence of Ytterbium Triflate Catalyst

S. Cauvin, F. Ganachaud

Sawamoto and coll. showed recently in a number of papers that pMOS would polymerize in suspension or emulsion with the help of high loads of a rare earth salt stable in water, namely ytterbium triflate (see structure on the right). The aim of this work was to implement the former catalyst in a miniemulsion formulation. Colloidal stability in the presence of such trivalent salt was difficult to reach, and required to use an electrosteric surfactant and low content of low molar mass polymer as an hydrophobe. The mechanism described before still applies to the system, but the catalyst slightly improved the polymerization rate and final average molar mass (2500 g/mol instead of 1200 g/mol). In some cases, high molar mass polymer chains were also observed, surely arising through a radical polymerization process, a point which remains to be elucidated.



Papers under submission

Tempered Anionic Polymerization of n-Butylcyanoacrylate in Miniemulsion I. Operating Conditions

C. Limouzin, A. Caviggia, F. Ganachaud, P. Hémery (submitted to Langmuir)

The manufacture and polymerization of stable n-butylcyanoacrylate miniemulsions were achieved in the presence of dodecylbenzenesulfonic acid (DBSA). This surfactant, by releasing protons at the interface, restrains the interfacial polymerization through (reversible) termination. Preliminary experiments showed that a certain quantity of DBSA was required to avoid the generation of long polymer chains through uncontrolled polymerization during sonication. In all experiments however, the final oligomer distribution was mainly composed of 3 or 4 units, equilibrium value due to interfacial polymerization/depolymerization events. Final particles quickly destabilize by Ostwald ripening of the partly water-soluble hydroxylated oligomers. Raising the pH *after sonication* however permitted the formation of longer chains and enhanced particle stability. Maximum molar masses of 1200 g/mol were however reached even in fast polymerization conditions, a critical chainlength for which oligomers lost their surface activity and thus stopped propagating.

2- Thesis

B. Charleux

Florence Mazuel	Design of new functional monomers to be used as crosslinking agents in latex films.
Patrice Castignolles	Pulsed laser polymerization (PLP) of acrylic esters.
Laurence Couvreur	PLP and controlled radical polymerization of acrylic acid.
Julien Nicolas	Nitroxide-mediated controlled radical polymerization in miniemulsion and emulsion.
Maggy Manguian	Application of controlled-radical polymerization to the synthesis of amphiphilic block and gradient copolymers.

F. Ganachaud

Séverine Cauvin	Cationic polymerization in miniemulsion using rare earth triflate catalysts.
Guillaume Palaprat	Mesogen cristal liquids prepared by ionic polymerization in emulsion in molecular imprinting technique.

3- List of recently published papers

B. Charleux

The Unique Behavior of Nitroxide Biradicals in Controlled-Radical Polymerization of Styrene

W. Huang, R. Chiarelli, B. Charleux, A. Rassat, J.-P. Vairon
Macromolecules 35, 2305 (2002)

Structural Characterization of Nitroxide-terminated Poly(n-butyl acrylate) prepared in bulk and miniemulsion polymerizations.
C. Farcet, J. Belleney, B. Charleux, R. Pirri
Macromolecules 35, 4912 (2002)

Nitroxide-Mediated Miniemulsion Polymerization of n-Butyl Acrylate : Synthesis of Controlled Homopolymers and Gradient Copolymers with Styrene.

C. Farcet, B. Charleux, R. Pirri
Macromol. Symp. 182, 249 (2002)

Synthesis of Water-Soluble Nitroxides and their Use as Mediators in Aqueous Phase Controlled Radical Polymerization.
W. Huang, B. Charleux, R. Chiarelli, L. Marx, A. Rassat, J.P. Vairon
Macromol. Chem. Phys. 203, 1715–1723 (2002)

Nanocrystalline Transition Metal Oxide Spheres with controlled multi-scale porosity.
D. Grosso, G. J. de A.A. Soler Illia, E. Crepaldi, B. Charleux, C. Sanchez (*Submitted*)

Use of a difunctional alkoxyamine initiator in the miniemulsion polymerization of n-butyl acrylate.
C. Farcet, B. Charleux, R. Pirri, O. Guerret
Am. Chem. Soc., Polym. Prepr. 43(2), 98-99 (2002)

Effect of chain transfer to polymer in nitroxide-mediated controlled free-radical polymerization of n-butyl acrylate.
C. Farcet, J. Belleney, B. Charleux
Am. Chem. Soc., Polym. Prepr. 43(2), 299-300 (2002)

F. Ganachaud

Synthesis of Monodisperse Poly(dimethylsiloxane) Micro- and Macroemulsions

M. Barrère, S. Capitao Da Silva, R. Balic, F. Ganachaud
Langmuir 18, 941 (2002)

Cationic Polymerization of p-Methoxystyrene in Miniemulsion
S. Cauvin, A. Sadoun, R. Dos Santos Costa, J. Belleney, F. Ganachaud, P. Hémery
Macromolecules *ASAP* (2002)

Determination of Alkoxyamine Concentrations in Nitroxyl-Mediated Styrene Polymerization Products

Mark E. Scott, J. Scott Parent,* Stephen L. Hennigar, Ralph A. Whitney, and Michael F. Cunningham

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Abstract

A fluorescence method is presented for measuring the concentration of TEMPO-terminated chains in polystyrene samples prepared by controlled free radical polymerization. Exchange of TEMPO with a naphthoyloxy derivative is used to fluorescence-label those alkoxyamine-terminated polymer chains that are capable of further styrene addition. Determination of the fluorophore concentration in the exchanged polymer provides an accurate assessment of the concentration of alkoxyamine-terminated chains within a given sample. Fractionation of samples by gel permeation chromatography and simultaneous analysis by differential refractive index and fluorescence provides a measure of the distribution of nitroxyl-terminated chain ends as a function of molecular weight. This method is demonstrated on a series of polystyrene samples synthesized under various polymerization conditions.

To appear in *Macromolecules*.

Interfacial Mass Transfer in Nitroxide-Mediated Miniemulsion Polymerization

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Abstract

A mathematical model has been developed to describe the interfacial mass transfer of TEMPO in a nitroxide-mediated miniemulsion polymerization (NMMP) system in the absence of chemical reactions. The model is used to examine how the diffusivity of TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) in the aqueous and organic droplet phases, the average droplet diameter and the nitroxide partition coefficient of influences the time required for the nitroxide to reach phase equilibrium under non-steady state conditions.

Our model predicts that phase equilibrium is achieved quickly ($<1\times10^{-4}$ s) in NMMP systems under typical polymerization conditions and even at high monomer conversions when there is significant resistance to molecular diffusion. The characteristic time for reversible radical deactivation by TEMPO was found to be more than ten times greater than the predicted equilibration times, indicating that phase equilibrium will be achieved before TEMPO has an opportunity to react with active polymer radicals. However, significantly longer equilibration times are predicted when average droplet diameters are as large as those typically found in emulsion and suspension polymerization systems, indicating that the aqueous and organic phase concentrations of nitroxide may not always be at phase equilibrium during polymerization in these systems.

Submitted to *Macromolecular Theory and Simulations*

Nitroxide-Mediated Radical Polymerization of Styrene in Miniemulsion: Model Studies of Alkoxyamine-Initiated Systems

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Abstract

A mathematical model has been developed to describe the behavior of the nitroxide-mediated miniemulsion polymerization (NMMP) of styrene initiated by alkoxyamine initiators. The model includes mechanisms describing reactions in the aqueous and organic phases, particle nucleation, the entry and exit of oligomeric radicals, and the partitioning of nitroxide and styrene between the aqueous and organic phases. The influence of nitroxide partitioning on the polymerization kinetics was examined by modeling systems initiated by the alkoxyamines BST and hydroxyl-BST; BST and hydroxyl-BST are benzoylstyryl radicals terminated by the nitroxides TEMPO and 4-hydroxyl-TEMPO, respectively.

Predicted monomer conversions, number average molecular weights and polydispersities were in agreement with experimentally measured values. Simulations

and mathematical analysis showed that the rate of styrene NMMP is not strongly influenced by the partitioning properties of TEMPO and 4-hydroxyl-TEMPO because of the complex interaction between reaction equilibrium, phase equilibrium, termination and thermal initiation. However, in the absence of styrene thermal initiation, nitroxide partitioning was found to have a significant influence on the polymerization kinetics. The model was also used to make quantitative estimates of: the population of active and dormant polymer radicals derived from both alkoxyamine initiators and thermal initiation; the population of dead polymer chains; and the number molecular weight distributions of living and dead polymer chains.

To appear in *Chemical Engineering Science*

Model Studies of Nitroxide-Mediated Styrene Miniemulsion Polymerization – Opportunities for Process Improvement

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Abstract

Modeling studies were performed to investigate how persulfate-initiated nitroxide-mediated styrene miniemulsion polymerizations are influenced by changes to the polymerization recipe. By manipulating the initial concentrations of potassium persulfate (KPS) and nitroxide, and the aqueous phase volume, trends in the predicted polymerization time, number average molecular weight, polydispersity and degree of polymer livingness were identified that indicate operating conditions for improved process performance. Specifically, our model predicts the existence of experimental conditions that simultaneously minimize polymer polydispersity and maximize the livingness of the polymer. The mechanisms responsible for the predicted trends were identified from the predicted molecular weight distributions of the living and dead polymer chains.

Submitted to *Macromolecular Theory and Simulations*

Nitroxide-Mediated "Living" Radical Polymerization of Styrene in Miniemulsion – Model Construction of Persulfate-Initiated Systems

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Abstract

Recently we have constructed a mechanistic model describing the nitroxide mediated miniemulsion polymerization (NMMP) of styrene at 135 ºC, using alkoxyamine initiators to control polymer growth (Ma et al., 2001b). The model has since been expanded to describe styrene NMMP at 135 ºC using TEMPO and the free radical initiator, potassium persulfate (KPS). The model includes mechanisms describing reactions in the aqueous and organic phases, particle nucleation, the entry and exit of oligomeric radicals, and the partitioning of nitroxide and styrene between the aqueous and organic phases. Predicted monomer conversions, number average molecular weights and polydispersities were in agreement with experimentally measured values. Model simulations revealed that for systems employing high ratios of TEMPO:KPS, the consumption of TEMPO by polymer radicals derived from KPS decomposition and styrene thermal initiation (using the accepted literature kinetic rates) is not sufficient to lower TEMPO concentrations to levels where polymer growth can occur. By accounting for the consumption of TEMPO by acid-catalyzed disproportionation, TEMPO concentrations are significantly reduced, allowing for accurate model predictions of monomer conversion, number average molecular weight and polydispersity at every experimental condition considered.

Submitted to *Chemical Engineering Science*

Living/Controlled Radical Polymerizations in Dispersed Phase Systems

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Abstract

Living/controlled radical polymerization provides a route to synthesizing materials with designed microstructure and narrow molecular weight distributions. A variety of living radical systems have been developed in recent years, and are based on either reversible termination (SFRP, ATRP) or reversible transfer mechanisms (RAFT, degenerative transfer). Application of living radical polymerization to heterogeneous systems such as emulsion and miniemulsion polymerization may provide process and economic advantages over the traditional homogeneous bulk and solution polymerizations. However adaptation of living radical chemistry to aqueous dispersions poses several challenges relating to maintaining effective control over the growth of living chains. These challenges originate from having two or even three phases in the reaction mixture, which can lead to issues related to phase partitioning of the controlling agent, transport of the controlling agent between phases, the role of aqueous phase kinetics, and the phenomena of particle nucleation and colloidal stability. This review examines recent progress in this area, with an emphasis on unresolved issues and future opportunities.

Progress in Polymer Science, 27 (2002) 1039-1067

Nitroxide-Mediated Styrene Miniemulsion Polymerization

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Abstract

Living radical polymerization of styrene was conducted in miniemulsion using TEMPO and the water-soluble initiator potassium persulphate (KPS). The effects of initiator concentration and the TEMPO:KPS ratio on conversion, molecular weight distribution and particle size were studied. The miniemulsion polymerizations exhibit similar characteristics to bulk living radical systems but with unique features attributable to the heterogeneous nature of the system. There is a strong interaction between the KPS concentration and the TEMPO:KPS ratio, and therefore the effects of changing either variable depend strongly on the value of the other variable. Initiator efficiencies are considerably higher than in conventional KPS-initiated styrene emulsion or miniemulsion polymerizations, while the average number of active radicals per particle ($\sim 10^{-2}$) is much lower. Aqueous-phase kinetics and nitroxide partitioning determine the number of chains initiated, and therefore also affect the polymerization rate and molecular weight.

Macromolecules (2002) 35, 59-66

Influence of Camphorsulfonic Acid in Nitroxide-Mediated Styrene Miniemulsion Polymerization

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Abstract

The rate accelerating effects of camphorsulfonic acid (CSA) on nitroxide-mediated styrene miniemulsion polymerization were studied. Polymerizations were initiated with benzoyl peroxide (BPO) as initiator and mediated with either 2,2,6,6 tetramethyl-1-piperidinyloxy (TEMPO) or 4-hydroxy 2,2,6,6 tetramethylpiperidinyloxy (OH-TEMPO). While CSA has been used to accelerate the rate in bulk nitroxide-mediated polymerizations, it has not been well-studied in emulsion/miniemulsion. With dispersed systems the effectiveness of CSA is likely to be affected by partitioning between the aqueous and organic phases. In styrene miniemulsion experiments performed over a range of conditions, the effect of adding CSA varied from negligible to significantly increasing the final conversion and molecular weight, depending on the nitroxide:BPO ratio. At a ratio of nitroxide:BPO=1.7, the effect of CSA addition is small, while the final conversion and molecular weight are dramatically enhanced by CSA addition when the nitroxide:BPO ratio is 3.6. CSA is most effective in enhancing rate and molecular weight when the initial free nitroxide concentration is higher. The magnitude of the rate and molecular weight enhancement was similar for TEMPO and OH-TEMPO, despite their differences in water solubility.

Journal of Polymer Science: Part A: Polymer Chemistry*, 40, 2828-2841 (2002)*

Nitroxide Mediated Living Radical Polymerization in Miniemulsion

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Abstract

The introduction of the aqueous phase into a living radical polymerization increases the complexity of the kinetics by creating the possibility of species partitioning between the aqueous and organic phases, and introducing aqueous phase reactions which could play a significant role particularly in chain initiation and/or particle nucleation. We have conducted a series of styrene miniemulsion polymerizations in which the solubility of initiator and nitroxide have been systematically varied. Experiments were run using either water-soluble (potassium persulphate) or oil-soluble (benzoyl peroxide) initiator, and either TEMPO or 4-hydroxy-TEMPO. These two nitroxides vary considerably in their water solubility. The effects of initiator and nitroxide solubility in water on conversion-time behaviour, molecular weight and initiator efficiency are presented.

Macromolecular Symposia (2001) 182, 273-282

Polystyrene Latexes Containing Poly(propyleneimine) Dendrimers

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Abstract

Polymerization of styrene in aqueous dispersions of sodium dodecyl sulfate (SDS) and the poly(propyleneimine) dendrimer DAB-*dendr*-$(NH_2)_{64}$ with initiation by potassium persulfate at 80 ^oC produced latexes with diameters in the range of 26-64 nm and coefficients of variation of diameters of less than 10%. Stable latexes were obtained starting with 1.0 to 4.0 molar ratios of SDS to dendritic primary amine end groups, 5.5 to 11 weight percent of SDS relative to styrene, and SDS concentrations below the critical micelle concentration in water at 25 ^oC. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) showed both individual particles and small clusters. TEM and AFM measurements of particle sizes agreed well. Dynamic light scattering measurements gave larger sizes and large polydispersities, presumably due to the presence of clusters.

Polystyrene Latexes Containing Dodecanamide-Modified Poly(propyleneimine) Dendrimers

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Abstract

Polymerization of styrene in aqueous dispersions of the dodecanamide derivative of poly(propyleneimine) dendrimer DAB-*dendr*-$(NH_2)_{64}$ and sodium dodecyl sulfate (SDS) produced stable latexes. Using initial SDS concentrations of 10 mM or less, molar ratios of SDS to dendrimer end groups ranging from 2.3:1 to 9.5:1, and less than 10 weight percent of SDS relative to styrene, the polystyrene latexes had diameters of 30-60 nm and coefficients of variation of diameters of less than 10% when measured by transmission electron microscopy. Higher concentrations of SDS gave more polydisperse latexes. The polystyrene latexes formed using SDS and the dodecanamide-modified dendrimer were almost the same size and polydispersity as those formed using SDS and the parent primary amine dendrimer DAB-*dendr*-$(NH_2)_{64}$.

Two-Dimensional Streptavidin Crystals on Giant Lipid Bilayer Vesicles

Ratanabanangkoon, P.; Gropper, M.; Merkel, R.; Sackmann, E.; Gast, A. P.;
Langmuir; (Article); 2002; 18(11); 4270-4276. DOI: 10.1021/la025568v
http://pubs.acs.org/journals/langd5/article.cgi/langd5/2002/18/i11/pdf/la025568v.pdf

Streptavidin was crystallized on giant bilayer vesicles (20-60 μm) in sucrose solution at various pH values. The streptavidin-coated vesicles exhibited unique roughened spherical and prolate ellipsoidal shapes, illustrating resistance to curvature of the two-dimensional crystals. Studies indicated that the spheroids and prolate ellipsoids correspond to different crystal morphologies. Through confocal microscopy, the various crystal morphologies on vesicle surfaces were observed under different solution conditions. Unlike two-dimensional (2D) streptavidin crystals grown in ionic buffer that assume the *P*1, *P*2, and *C*222 lattices at pH 4, 5.5, and 7, respectively (Wang et al. *Langmuir* **1999**, *15,* 1541), crystals grown in sucrose with no added salt show only the lowest density *C*222 lattice due to strong electrostatic interactions.

Dendritic-Linear Miktoarm Star Polymers from Orthogonal Protected Initiators

Glauser, T.; Stancik, C. M.; Moller, M.; Voytek, S.; Gast, A. P.; Hedrick, J. L.;
Macromolecules; (Article); 2002; 35(15); 5774-5781. DOI: 10.1021/ma0122369
http://pubs.acs.org:80/journals/mamobx/article.cgi/mamobx/2002/35/i15/pdf/ma0122369.pdf

The synthesis of miktoarm dendritic-linear star copolymers in a tandem "core-in"/"core-out" approach is described. This synthetic approach is enabled by rational design and synthesis of an orthogonal protected compound containing six sites arranged in an alternating fashion for attachment of dendrimers and atom transfer radical polymerization of linear polymer chains. The judicious choice of the dendrimer surface functionality coupled with the properties of the monomer used in the linear chain allows the creation of amphiphilic molecules capable of supramolecular assembly. 1H NMR and SEC studies of the block copolymers confirmed that the targeted polymer structures were achieved with low polydispersities and good yields. The nature and the size of the arms and dendrons had a significant influence on the hydrodynamic radii (Rh) measured by dynamic light scattering. Some of these macromolecules microphase-separated after annealing.

Surface Plasmon Resonance/Surface Plasmon Enhanced Fluorescence: An Optical Technique for the Detection of Multicomponent Macromolecular Adsorption at the Solid/Liquid Interface

Roy, S.; Kim, J.-H.; Kellis, J. T., Jr.; Poulose, A. J.; Robertson, C. R.; Gast, A. P.;
Langmuir; (Article); 2002; 18(16); 6319-6323. DOI: 10.1021/la025578w
http://pubs.acs.org/journals/langd5/article.cgi/langd5/2002/18/i16/pdf/la025578w.pdf

We describe an optical technique for the measurement of macromolecular adsorption at the solid/liquid interface when multiple species are present. The technique combines surface plasmon resonance (SPR) with simultaneous surface plasmon enhanced fluorescence (SPEF). The relative ease of construction and linear correlation between

SPR and SPEF signals make the technique amenable for coadsorption studies or multiple ligand binding experiments. Here, we demonstrate the utility of the technique with a biotin/avidin/BSA "sandwich" experiment. We then apply SPR/SPEF for the simultaneous monitoring of enzyme adsorption and substrate cleavage of a protease interacting with a substrate surface.

Protease Adsorption and Reaction on an Immobilized Substrate Surface

Kim, J.-H.; Roy, S.; Kellis, J. T., Jr.; Poulose, A. J.; Gast, A. P.; Robertson, C. R.; Langmuir; (Article); 2002; 18(16); 6312-6318. DOI: 10.1021/la025579o
http://pubs.acs.org/journals/langd5/article.cgi/langd5/2002/18/i16/pdf/la025579o.pdf

Enzymatic reactions with surface-bound substrates present an interesting problem in biomolecular surface science, as they require us to consider traditional enzyme kinetics in the context of protein adsorption. These reactions are important in such applications as detergent enzyme additives, food processing, and contact lens cleaning. We study the interaction of a serine protease (subtilisin) with an immobilized substrate (bovine serum albumin) surface through the simultaneous use of surface plasmon resonance and surface plasmon enhanced fluorescence techniques. We measure adsorbed enzyme concentrations and substrate cleavage rates in situ and compare the reactivities with those in solution. By varying the ionic strength of the reaction environment and studying several single point mutations of subtilisin, we find the adsorption behavior of the enzyme is strongly influenced by its electrostatic interactions with the charged bovine serum albumin surface. The surface reactivity of each of the mutants is coupled to its adsorption properties. On the basis of these findings, we propose a modified Michaelis-Menten enzyme surface adsorption and reaction model.

Unpublished Papers

Mechanics of Streptavidin-Coated Giant Lipid Bilayer Vesicles: A Micropipette Study

Pasut Ratanabanangkoon, Michael Gropper, Rudolf Merkel, Erich Sackmann, and Alice P. Gast

To understand the effects of a crystalline protein layer on bilayer properties, we studied the mechanical properties of avidin and streptavidin coated giant lipid bilayer vesicles. The giant vesicles(20-60 mm) are made from a mixture of SOPC and biotinylated phospholipids via electroformation. Using micropipette manipulation, we showed that the presence of a monomolecular layer of noncrystalline avidin on the vesicle surface increases the membrane bending rigidity but does not significantly alter the elastic area expansion modulus of the vesicle. When the vesicles were coated with streptavidin, the protein crystallizes on the bilayer surface, resulting in a rigid polycrystalline membrane. These vesicles display unique roughened spherical or prolate ellipsoidal shapes depending on the differences in crystal morphologies. Upon aspiration with micropipettes, the vesicles first showed rapid permanent deformation at low strain, followed by a slower viscoelastic response above a certain threshold. Despite their extremely rigid appearance, the existence of a polycrystalline shell does not increase the toughness of streptavidin-coated vesicles above that of uncoated vesicles. The origin of these properties can be traced to the unique ligand-receptor interactions between streptavidin and biotinylated phospholipids in the bilayer membrane. The findings offer greater understandings of complex phenomena involving crystalline protein layers on the surface of cell membranes in addition to providing information for the development of various applications involving the immobilization of functionalized molecules on lipid bilayer substrates.

The Effects of Ionic Strength on Two-Dimensional Streptavidin Crystallization

Pasut Ratanabanangkoon, Alice P. Gast

Two-dimensional (2D) streptavidin crystallization was performed on giant lipid bilayer vesicles and lipid monolayers at the air-water interface under extremely low ionic strength conditions. Unlike the variety of 2D crystals grown in high ionic strength buffers at different pH values, strong electrostatic repulsions favored the low density C222 crystal form. Both the crystals grown on giant vesicles and those on lipid monolayers show the same crystal structure and share similar crystallization trends despite the difference in surface geometries. When the ionic strength of the crystallization solution is progressively increased at pH 4, we observe a transition from C222 to the denser P1 space group commonly seen in high ionic strength conditions at this pH. We have also shown that we can produce similar crystallization transition through global change in electrostatic interactions of the streptavidin molecules by altering the solution ionic strength, the solution pH, or through local changes from point mutations of specific amino acids within the protein molecule.

The impact of core architecture on solution properties of dendrimer-like star copolymers

Cheryl M. Stancik, John A. Pople, Peter Lindner, James L. Hedrick, and Alice P. Gast

We present a small-angle neutron scattering (SANS) study of a series of dendrimer-like star copolymers investigated in solution. Each copolymer consists of a highly branched core with linear polymer chains emanating from the outermost generation to create a star-like copolymer. This series allow us to assess the effects of the branching architecture within the copolymer core. We fit dilute solution scattering data to models to obtain expressions for the form factor and parameters that describe the single molecule conformations. These results are combined with the semi-dilute data in order to obtain experimental structure factors for each molecule. From the structure factors, we see evidence of liquid-like structuring in some copolymers. Both the dilute and semi-dilute analyses show that the architectural features of these isomeric copolymers have an impact on both the conformation of and interactions between these molecules in solution.

Conference Presentations

The Physical Properties of Naturally Occurring Polymers

Paulina A. Achurra, John A. Pople, Craig J. Hawker, Channing R. Robertson, and Alice P. Gast

Poster Presentation, Gordon Conference on Colloidal, Macromolecular & Polyelectrolyte Solutions (Feb. 2002)

We aim to develop techniques to understand the structure of proanthocyanidins (PAs), a class of highly branched naturally occurring polymers, to further relate architecture to their physical and biophysical properties. It is known PAs interact with salivary proteins and that such interactions are critical to certain organoleptic properties. These interactions are in turn believed to be dependent on the degree of polymerization and architecture [or branching structure] of the polymer. To reach this goal we have studied model polystyrene (PS) polymers of highly defined yet architecturally distinct structures allowing us to identify the important structural characteristics of different architectures that are relevant to the PA system. We have focused on the study of a series of three PS polymers of star-like architecture, which are characterized by different molecular weights and number and length of arms. These model systems possess the types of variable architectural signatures we intend to examine when addressing the more complex proanthocyanidin systems. The stars were studied in solution using dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS). The SAXS studies show the distinctive features for a star architecture, which arises due to their unique radial density profile. The scaling exponent for the PS polymer system in THF was determined to be 0.6, which is consistent with THF being a good solvent for PS. Hydrodynamic radii and radii of gyration were determined by DLS and SAXS, respectively, allowing us to clearly differentiate the three star polymers. This study shows that scattering techniques are extremely valuable tools to study macromolecular architecture.

Flexural Rigidity Measurements of Cross-Linked Chains of Magnetic Particles

Sibani Lisa Biswal, Alice Gast

Poster Presentation, Gordon Conference on Colloidal, Macromolecular & Polyelectrolyte Solutions (Feb. 2002)

Introduction

Magnetorheological fluids form reversible chains by acquiring dipole moments in the presence of an external magnetic field. By physically crosslinking paramagnetic colloidal particles, a magneto-responsive microstructure can be created.

Crosslinking Magnetic Beads

We create 1 μm magnetic microspheres permanently attached together with streptavidin-biotin chemistry. Streptavidin is a tetrameric protein with a high affinity for the molecule biotin. Streptavidin coated microspheres are placed in a flow cell and a magnetic field is applied, causing the particles to form chains. Then a solution of polymeric linkers of bis-biotin-polyethylene glycol molecules is added in the presence of the field. This method is successful in creating flexible and linked paramagnetic chains. We attach 3μm non-magnetic polystyrene microspheres at the ends of the chains to serve as "handles" for the optical trapping experiments since the magnetic particles are difficult to trap directly.

Micromechanics

Optical trapping is a powerful tool that can be used to study the mechanical properties of these permanently linked chains. It uses a highly focused laser light to trap and manipulate microscopic objects. We calibrate the trapping force using Stokes' flow past trapped spheres. Our current laser arrangement produces traps of 1-20 picoNewton strength. The optical trapping experiments allow us to manipulate these chains to study their flexibility and deformation.

The flexural rigidity or bending stiffness used to describe the chain's resistance to bending forces. Three different experiments are done to determine the flexural rigidity of the chains. In the first experiment, the thermally driven fluctuations in the shape of the chain are analyzed to determine its flexural rigidity. The next experiment involves bending the chain by manipulation with optical traps. By knowing the deflection and the magnitude of the force acting on the bent chain, the flexural rigidity can be determined. The last experiment shows a chain's linear spring response to elongation, providing a measure of the force versus extension and flexural rigidity. These experiments show how the bending and stretching behavior differ for these chains.

Two Dimensional Streptavidin Crystals on Giant Lipid Bilayer Vesicles

Poe Ratanabanangkoon, Michael Gropper, Rudolf Merkel, Alice P. Gast
Poster Presentation, Gordon Conference on Colloidal, Macromolecular &
Polyelectrolyte Solutions (Feb. 2002)

We studied the protein streptavidin crystallized on the surface of giant (20-60 microns) lipid bilayer vesicles using confocal microscopy and micropipette methods. The presence of a rigid crystalline shell altered both the morphology and the mechanical properties of the bilayer vesicles. Morphologically, the vesicles take on either roughened spherical or prolate ellipsoidal shapes due to differences in crystal morphologies. The observed vesicle shapes are indicative of the anisotropic bending rigidity and resistance to curvature of the two dimensional (2D) streptavidin crystals. The vesicles also showed unique mechanical properties such as the presence of permanent deformation when slightly perturbed, followed by a slower viscoelastic response at higher strain. In this study, we seek to understand the effects of a crystalline protein layer on bilayer properties. The findings may provide information on many complex phenomena involving crystalline protein layers on the surface of cell membranes.

Novel polymer architectures investigated with scattering techniques

Cheryl M. Stancik, John A. Pople, James L. Hedrick, and Alice P. Gast

Poster Presentation, Gordon Conference on Colloidal, Macromolecular &
Polyelectrolyte Solutions (Feb. 2002)

In order to investigate the effects of polymer architecture on their intermolecular interactions we studied a series of novel dendrimer-like star polymers and copolymers. We performed small angle x-ray and neutron scattering experiments on solutions of these polymers at moderate concentrations. A series of six isomeric polymers was prepared from poly(e-caprolactone) (PCL) using synthetic techniques that allowed for carefully defined polymer architectures. The isomeric PCL polymers within this series differ only in the placement of the branching junctures and the length of the polymer chains that connect these branches. Small angle x-ray scattering (SAXS) studies of these polymers at concentrations ranging from dilute to near the overlap concentration illustrated the impact the position of the branching junctures and the branch lengths impart on the intermolecular interactions of these polymers. A copolymer series was created by replacing the outermost surface dendron with linear poly(methylmethacrylate) (PMMA) chains. Partial deuteration of the PMMA blocks allowed the PCL cores of these block copolymers to be highlighted in a core contrast small angle neutron scattering (SANS) study. The PCL-PMMA dendrimer-like star copolymers were studied at varying concentrations yielding information about the intermolecular interactions of the PCL cores. Structure factor data from both the SANS and SAXS studies provided information about the intermolecular spacing of the liquid-like structure and the effects of the PMMA chains on this structure.

A SANS investigation of the structure and interactions of dendrimer-like star copolymer architectures in solution

Cheryl M. Stancik, John A. Pople, James L. Hedrick, and Alice P. Gast

Oral Presentation, American Conference on Neutron Scattering (June 2002)

We present a small-angle neutron scattering (SANS) study of a series of dendrimer-like star copolymers investigated in solution. These studies allow us to assess the effects of architecture on the conformation of individual copolymer molecules in the dilute regime and interactions of these molecules near the overlap concentration. Each copolymer within the series consists of a highly branched core prepared from poly(□-caprolactone) (PCL). Emanating from the outermost generation of the PCL cores, partially deuterated linear poly(methylmethacrylate) (PMMA) chains are attached to create a star-like copolymer. This series allows us to consider the effects of branching architecture within the PCL core and arm architecture of the PMMA star branches. Using dilute solution results, we fit the data to models to obtain expressions for the form factor and parameters that describe the single molecule conformations. These results are applied to the semi-dilute data in order to obtain experimental structure factors for each molecule. From the structure factors, we see evidence of liquid-like structuring in some copolymers. We find that these copolymers adopt a uniform distribution. Both the dilute and semi-dilute analyses show that the different architectural features of these isomeric copolymers have an impact on both the conformation and interactions of these molecules in solution.

Rotating Magnetic Chains

Sibani Lisa Biswal, Alice P. Gast

Oral Presentation, SmallTalk Conference (July 2002)

Introduction

Magnetorheological fluids form reversible chains by acquiring dipole moments in the presence of an external magnetic field. By physically crosslinking paramagnetic colloidal particles, a magneto-responsive microstructure can be created for microfluidic applications.

Crosslinking Magnetic Beads

We create chains of 1μm magnetic microspheres permanently attached together with streptavidin-biotin chemistry. Streptavidin is a tetrameric protein with a high affinity for the molecule biotin. Streptavidin coated microspheres are placed in a flow cell and a magnetic field is applied, causing the particles to form chains. Then a solution of polymeric linkers of bis-biotin-polyethylene glycol molecules is added in the presence of the field. This method is successful in creating flexible and linked paramagnetic chains. These chains can vary in length on the order of tens of microns.

Rotating Magnetic Chains

The stability of these magnetic structures is studied in microchannels under coupled magnetic and fluid flow fields. In the presence of a magnetic field, the chains stiffen and orient in the direction of the field applied. When the field is removed, the chains relax and follow the fluid flow profile. When the chains are placed in a rotating magnetic field they begin to spin. The small size of these chains make then ideal for use as micro-stirrers in microfluidic channels.

Contribution to the IPCG Newsletter from the Key Centre for Polymer Colloids

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The Key Centre for Polymer Colloids currently comprises about 25 researchers. The Director is Professor Robert G Gilbert, Dr Brian S Hawkett is Development Manager, Dr Christopher M Fellows is Scientific Projects Officer, Jelica Strauch is Laboratory Manager, plus a team of graduate students, researchers and visiting scholars from around the world. More information about the Centre can be found on the website given above.

Papers submitted or in press

Entry in Emulsion Polymerization: Effects of Initiator and Particle Surface Charge. KY van Berkel, GT Russell and RG Gilbert, submitted.

The rate coefficient for radical entry into latex particles in emulsion polymerizations is measured for styrene systems in which the entering species are anionic (from persulfate) and cationic (from 2,2´-azobis-(2-methylpropionamidine) dihydrochloride, or V-50). These entry rate coefficients ρ are obtained by measuring rates in seeded emulsion polymerizations where the seeds have either cationic or anionic groups on the surface; 'zero-one' conditions are employed, because these offer the advantage that particle size is sufficiently small (≈ 70 nm diameter) that termination is not rate-determining. Data comprise steady-state rates with chemical initiator, combined with loss rates obtained using γ-radiolysis initiation and following the relaxation behavior following removal from the radiation source. Values for ρ as a function of initiator concentration can be meaningfully compared for different initiators through the dependence of initiator efficiency f_{entry} on primary radical generation rate (radical flux). For the anionic latex, this dependence is seen to differ depending on the nature of the initiator used. This may be explained by the entry model (Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629) wherein the rate-determining steps in entry are assumed to be only aqueous-phase propagation and termination to form surface-active z-meric oligomeric radicals; entry is solely by z-mers, for which actual entry into the particle is so fast as not to be rate-determining. The cationic latex shows a high rate of spontaneous initiation, which can be explained in terms of amidino radical chemistry; this can be reduced by heat treatment. Accurate f_{entry} values are obtained using the heat-treated cationically-stabilized latex for seeded studies. The f_{entry} data are also consistent with the model for both cationic and anionic species entering the cationic latex. Values of z so inferred (≈ 2 for persulfate, ≈ 1 for amidinium) can be understood in terms of the hydrophobic free energy of these species. The results refute alternative models in the literature that entry may be controlled by double-layer (colloidal) interactions, surfactant displacement or diffusion control.

Molecular weight and functional end group control by RAFT polymerization of a bi-substituted acrylamide derivative. F. D'Agosto, R. Hughes, M.-T. Charreyre, C. Pichot and RG Gilbert, submitted.

Controlled radical polymerization of the bi-substituted acrylamide derivative N-acryloylmorpholine (NAM) has the potential to yield polymers grafted to latex particles to which can be attached a wide range of functionalities with applications in molecular biology and biomedicine. The controlled polymerization of NAM using reversible addition-fragmentation chain transfer (RAFT) is performed using two new chain transfer agents S=C(Z)–SR bearing the same functional propionic acid group (R) and two different Z groups, benzyl (CTA 1) and phenyl (CTA 2). RAFT polymerization of NAM mediated by CTA 1 is very fast (>80% conversion in less than half an hour at 65˚C). The linear evolution of $\overline{M}_n$ and the low polydispersity indices ($\overline{M}_w / \overline{M}_n < 1.2$) are in accord with the expected characteristics of a living polymerization. CTA 2 leads to broader $\overline{M}_w/\overline{M}_n$s (< 1.4). The resulting CTA-capped polymers were further polymerized to yield an amphiphilic polyNAM-*block*-polystyrene. These α,ω-functionalized polyNAM chains were characterized by ^{1}H NMR and MALDI-ToF mass spectrometry.

Effective Ab Initio Emulsion Polymerization Under RAFT Control. CJ. Ferguson, RJ Hughes, BTT Pham, BS Hawkett, RG Gilbert, AK Serelis and CH Such, submitted.

A new method is developed whereby RAFT controlled radical polymerization can be implemented in an *ab initio* emulsion polymerization, avoiding the often-encountered problems of loss of colloidal stability and of molecular weight control, and without any oily layer. Earlier studies [SW Prescott, MJ Ballard, E Rizzardo and RG Gilbert. *Macromolecules,* **35**, 5417-25 (2002)] show that these problems can be avoided in a seeded system using a hydrophobic RAFT agent (transported to the particles using acetone, which is subsequently removed); this observation is consistent with the difficulties encountered in simple application of RAFT in *ab initio* emulsion polymerization arising from droplet nucleation. The new strategy for *ab initio* systems is to use an amphipathic RAFT agent which can function in both aqueous and organic phases to grow acrylic acid to an appropriate degree of polymerization (~5) in the water phase. Controlled amounts of a hydrophobic monomer are then added until a degree of polymerization is attained such that rigid micelles form spontaneously. These effectively function as seeds which are then the locus of subsequent growth, with continued feed of the hydrophobic monomer. In these systems, good molecular weight control is maintained, without loss of colloidal stability or formation of an oily layer.

Polyaniline. Preparation of a conducting polymer (IUPAC technical report). J. Stejskal, RG Gilbert, *Pure and Applied Chem.* **2002**, *74*, 857-67.

Eight persons from five institutions in different countries carried out polymerizations of aniline following the same preparation protocol. In a “standard” procedure, aniline hydrochloride was oxidized with ammonium peroxydisulfate in aqueous medium at ambient temperature. The yield of polyaniline was higher than 90 % in all cases. The electrical conductivity of polyaniline hydrochloride thus prepared was 4.4 ± 1.7 S cm^{-1} (average of 59 samples), measured at room temperature. A product with defined electrical properties could be obtained in various laboratories by following the same synthetic procedure. The influence of reduced reaction temperature and increased acidity of the polymerization medium on polyaniline conductivity were also addressed. The conductivity changes occurring during the storage of polyaniline were monitored. The density of polyaniline hydrochloride was 1.329 g cm^{-3}. The average conductivity of corresponding polyaniline bases was 1.4×10^{-8} S cm$_{-1}$, the density being 1.245 g cm^{-3}. Additional changes in the conductivity take place during storage. Aging is more pronounced in powders than in compressed samples. As far as aging effects are concerned, their assessment is relative. The observed reduction in the conductivity by ~10 % after more than one-year storage is large but, compared with the low conductivity of corresponding polyaniline (PANI) base, such a change is negligible. For most applications, an acceptable level of conductivity may be maintained throughout the expected lifetime.

Synthesis of Latices with Polystyrene Cores and Poly(Vinyl Acetate) Shells. 1. Use of Polystyrene Seeds. CJ Ferguson, GT Russell, RG Gilbert. *Polymer*, in press.

Strategies for avoiding secondary particle formation in seeded emulsion polymerisation, based on a simple model for particle nucleation [Morrison, B. R.; Gilbert, R. G. Macromol. Symp. 1995, 92, 13], are discussed and exemplified in the context of growing latex particles with polystyrene cores and poly(vinyl acetate) shells. With a polystyrene seed of unswollen radius 44 nm, core-shell polymerisation was easily achieved. However, when the same recipes were used with a polystyrene seed of unswollen radius 200 nm, excessive new particle formation occurred and no poly(vinyl acetate) shells could be detected. A wide selection of the suggested strategies for overcoming this were implemented, but always either extensive secondary nucleation occurred or the system became colloidally unstable. These results are in full accord with the predictions of the simplified nucleation model.

RAFT in emulsion polymerization: what makes it different. SW Prescott, MJ Ballard, E Rizzardo, RG Gilbert. *Aust. J. Chem*., **55**, 415-24 (2002).

Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization techniques have been the focus of a great deal of recent work, particularly in their application to emulsion polymerization, which is the method of choice for implementing most free-radical polymerizations on an industrial scale. RAFT/emulsion polymerizations have considerable technical potential: to “tailor-make” material properties, to eliminate added surfactant from surface coatings, and so on. However, considerable difficulties have been experienced in using RAFT in emulsion polymerization systems. Here, progress in the application of RAFT techniques to emulsion polymerization is reviewed, summarizing the difficulties that have been experienced and mechanisms that have been postulated to explain the observed behaviour. Possible origins of the difficulties in implementing RAFT in emulsion polymerizations include polymerization in droplets, water sensitivity of some RAFT agents, slow transport of highly hydrophobic RAFT agents across the water phase, and surface activity of some RAFT agents.

Critically evaluated termination rate coefficients for free-radical polymerization, 1. The current situation**.** M Buback, M Egorov, RG Gilbert,V Kaminsky, OF Olaj, GT Russell, P Vana, G Zifferer. *Macromol. Chem. Phys.,* in press.

This is the first publication of an IUPAC-sponsored Task Group on “Critically evaluated termination rate coefficients for free-radical polymerization.” The paper summarizes the current situation with regard to the reliability of values of termination rate coefficients kt. It begins by illustrating the stark reality that there is large and unacceptable scatter in literature values of kt, and it is pointed out that some reasons for this are relatively easily remedied. However, the major reason for this situation is the inherent complexity of the phenomenon of termination in free-radical polymerization. It is our impression that this complexity is only incompletely grasped by many workers in the field, and a consequence of this tendency to oversimplify is that misunderstanding of and disagreement about termination are rampant. Therefore this paper presents a full discussion of the intricacies of kt: sections deal with diffusion control, conversion dependence, chain-length dependence, steady state and non-steady state measurements, activation energies and activation volumes, combination and disproportionation, and theories. All the presented concepts are developed from first principles, and only rigorous, fully-documented experimental results and theoretical investigations are cited as evidence. For this reason it can be said that this paper summarizes all that we, as a cross-section of workers in the field, agree on about termination in free-radical polymerization. Our discussion naturally leads to a series of recommendations regarding measurement of kt and reaching a more satisfactory understanding of this very important rate coefficient.

Operation of Semi-batch Emulsion Polymerisation Reactors: Modelling, Validation and Effect of Operating Conditions. J. Zeaiter, J.A Romagnoli, G.W. Barton, V.G. Gomes, B.S. Hawkett and R.G. Gilbert. *Chem. Eng. Sci.*, **57**, 2955-69 (2002).

A detailed dynamic model was developed for a styrene emulsion polymerisation semi-batch reactor to predict the evolution of the product particle size distribution (PSD) and molecular weight distribution (MWD) over the entire range of monomer conversion. A system exhibiting zero-one kinetics was employed, with the model comprising a set of rigorously developed population balance equations to predict monomer conversion, PSD and MWD. The modelling equations included diffusion-controlled kinetics at high monomer conversion where the transition from the zero-one regime to a pseudo-bulk regime occurs. The model predictions were found to be in good agreement with experimental results. Both particle growth and the PSD were found to be strongly affected by the monomer feedrate. Reactor temperature had a major influence on the MWD which was, however, insensitive to changes in the monomer feedrate. These findings were confirmed experimentally. As a result, it seems reasonable to propose that the use of the monomer feedrate to control the PSD and the reactor temperature to control the MWD are appropriate in practical situations. Consequently, an optimal monomer feed trajectory was developed off-line (using the validated reactor simulation) and verified experimentally by producing a polymer with specific PSD characteristics.

Emulsion polymerization of vinyl *neo*-decanoate, a “water-insoluble” monomer. H de Bruyn, CM Miller, DR Bassett and RG Gilbert. *Macromolecules,* (ASAP reference DOI 10.1021/ma020101c).

> *Abstract:* Rate and particle size data for the emulsion polymerization of vinyl *neo*-decanoate, where inhibitor/retarder effects are obviated through rigorous purification, can be quantitatively fitted by conventional mechanisms for particle formation and growth, even though the monomer has a very low water solubility. That is: radical entry is by an oligomeric radical (*z*-mer) arising from aqueous-phase propagation at a critical degree of polymerization (*z* between 1 and 2 for this monomer) where the species becomes surface-active, and radical loss is by transfer to a species which desorbs into the aqueous phase and eventually terminates (after re-entry into another particle) rather than undergoing further propagation. Particle formation is by a *z*-mer entering a micelle. These hypotheses are consistent with γ-relaxation data which give direct information on radical loss.

Water-binding and oxygen permeability in poly(vinyl alcohol) films. L Lien, CM Fellows, L Copeland, BS Hawkett, RG Gilbert. *Aust. J. Chem.,* in press.

> Abstract: The measurement and interpretation of isotherms for sorption of water onto, and oxygen permeability of, polymer substrates are important for designing polymers in applications such as agricultural seed coatings. Moisture sorption isotherms were measured for a series of poly(vinyl alcohol-*co*-vinyl acetate) substrates of different composition at 25°C. The data were fitted to the D’Arcy-Watt model, which gave physically reasonable values for parameters related to the strength of monolayer adsorption to high affinity sites on the substrate and the number of sites for secondary water absorption per unit mass. The oxygen permeability of poly(vinyl alcohol) films was found to be a function only of the water content of the films, with no other obvious contributing factors. Marked differences were seen in the populations of ‘bound’ and ‘unbound’ water characterised by $_1$H-NMR and moisture sorption isotherm fitting. There was no correlation of oxygen permeability with ‘bound’ or ‘unbound’ water measured by any means, suggesting that there is a continuum of water environments within the materials.

The following publications have appeared since the previous Newsletter

The interactions of amphiphilic latexes with surfaces: the effect of surface modifications and ionic strength. SW Prescott, CM Fellows, RF Considine, CJ Drummond, RG Gilbert. *Polymer*, **43**, 3191-8, 2002.

Successful use of RAFT techniques in seeded emulsion polymerization: living character, raft agent transport and rate of polymerization. SW Prescott, MJ Ballard, E Rizzardo and RG Gilbert. *Macromolecules,* **35**, 5417-25 (2002).

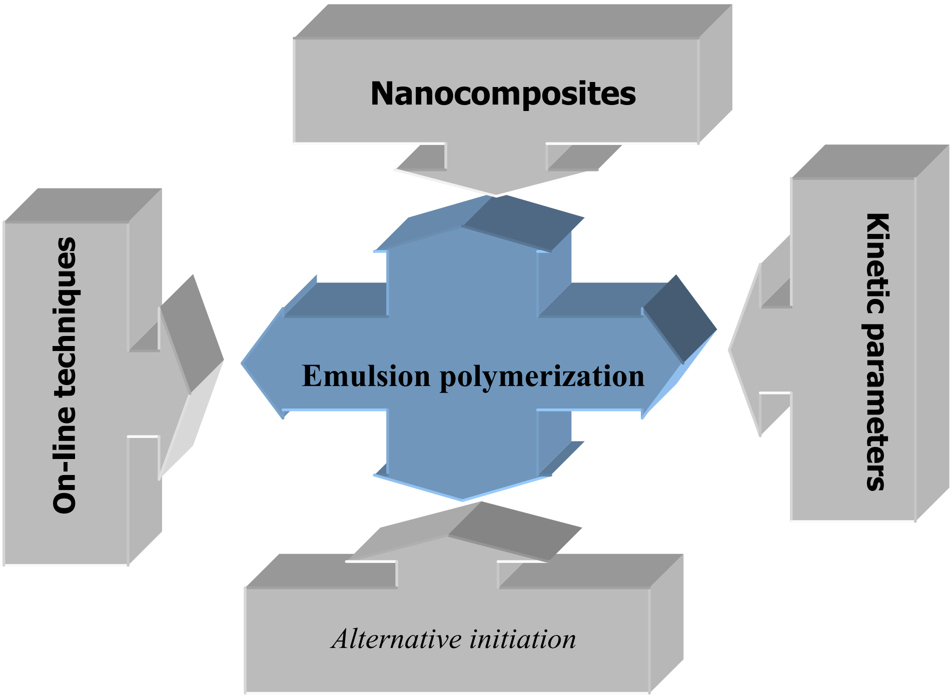
Effect of branching and molecular weight on the viscoelastic properties of butyl acrylate. C Former, J Castro, CM Fellows, RI Tanner and RG Gilbert. *J. Polym. Sci. A Polym. Chem. Ed.,* **40**, 3335-49 (2002).

Modelling secondary particle formation in emulsion polymerisation – application to making core-shell morphologies. CJ Ferguson, GT Russell and RG Gilbert. *Polymer*, **43**, 4545-55 (2002).

Effect of purification methods on rice starch structure. H. Chiou, M. Martin, M. Fitzgerald. *Starch*, **54**, 415-20 (2002).

Contribution of the researchgroup Van Herk/Meuldijk, Eindhoven University of Technology The Netherlands

In the year 2001 Prof. Anton German retired. He is still active in the foundation emulsion polymerization. Prof. Alex van Herk is continuing the research in the field of emulsion polymerization and related topics (as shown in the scheme).
A small account of results obtained in 2002 is given below, followed by a list of publications.



Process strategies have been developed to obtain homogeneous copolymers or copolymers of well-defined heterogeneity. It was shown that copolymers with the same average chemical composition but different CCDs show dramatic differences in mechanical properties.
The implementation of *on-line Raman spectroscopy* in emulsion copolymerization has been successful for several systems. Pulses of radicals (through light or electron beam) have been used to obtain the *local monomer concentration* in for example latices and vesicles.

Mechanistic studies towards the elucidation of RAFT, CCTA and ATRP have supported the development of strategies to synthesize block copolymers, both in homogeneous and heterogeneous systems.

Living radical polymerizations were studied, since these may open very interesting perspectives for the preparation of (multi)block copolymers and in preparing narrow molar mass distributions. There is a strong incentive to apply 'living' radical polymerization (LRP) in water based emulsion polymerizations to produce *block copolymer latexes* in a cost-efficient way. LRP methods based on *dithiocompound reversible chain transfer agents*, such as MADIX and RAFT appear to be the most significant breakthrough in the field next to *Atom Transfer Radical Polymerization*

(ATRP). Both mechanisms have been implemented in emulsion polymerizations and have led to successful reactions and interesting morphologies.
The replacement of conventional chain transfer agents by catalytic chain transfer agents in emulsion polymerization has been investigated.

Through *electron beam initiation* optically transparent latices have been prepared without high levels of surfactant as normally necessary. The bio-optical applications of these latices are currently under investigation together with the biomedical industry.

Latex production is in general carried out in large scale (semi-) batch processes. Research in the field of (semi-) batch processes was focused on the influence of operation and scale on the particle nucleation process. We have demonstrated that scale sensitivity of emulsion polymerisation reactors is mainly governed by the quality of emulsification which has a large influence on the course of the nucleation process and so on the particle size distribution of the product. We have also demonstrated that the rate of heating of the reaction mixture at the beginning of the emulsion polymerisation process is an essential parameter for the particle size distribution of the final product.

We have shown that the pulsed packed column (PPC) is a very useful reactor for the production of seed particles. The pulsed packed column combines low net flow rates with intensive radial mixing. Oscillation free production of seed latex without fouling is possible in the PPC. Homogeneous copolymers and copolymers with a bimodal chemical composition distribution can be produced in the PPC and a series of CSTRs
Staff members active in emulsion polymerization:
Dr. Ir. Bas Pierik
Dr. Jan Meuldijk
Ing. C. Göttgens
Dr. Ir. Jos Laven
At the moment 6 PhD’s and 1 post-doc are active in the field

Publications in the area of emulsion polymerization 2002

Handbook of radical polymerization, chapter 6 heterogeneous systems
A.M. van Herk, M. Monteiro p301-331 2002, ed. K. Matyjaszewski and T.P. Davis

Reduction of residual monomer in latex products by enhanced polymerization and extraction in supercritical carbon dioxide
M. Kemmere, M. van Schilt, M. Cleven, A.M. van Herk and J. Keurentjes
Ind. Eng. Chem. Res, 2002, 41, 2617-2622

Raman spectroscopy of polymer latexes
Mark van den Brink, Michel Pepers and Alex M. van Herk
J. Raman Spectrosc., 33 (2002) 264-272

Polymerization of styrene in DODAB vesicles: A small-angle neutron scattering study
Martin Jung, Brian H. Robinson, David C. Steytler, Anton L. German and Richard K. Heenan
Langmuir, 18 (2002) 2873-2879

Auke Snijder, Bert Klumprman and Rob van der Linde
Kinetics of heterogeneous atom transfer radical polymerisation of methyl methacrylate
Macromolecules, 35 (2002) 4785-4790

The morphology and adhesive force of natural rubber latex films by atomic force microscopy

C.C. Ho and M.C. Khew

ACS Symposium Series 801 “Polymer Colloids”, (E.S. Daniels, E.D. Sudol, M.S. El-Aasser, ed.), American Chemical Society, Washington, DC, p239-259 (2002).

ABSTRACT

Commercial natural rubber latex concentrate is used almost exclusively in the production of rubber-dipped goods, the bulk of which is in the form of gloves.
When a ‘former’ is dipped into the latex, a latex film is formed after the water evaporates and the particles come into contact and fuse together. Any factors that hinder good film formation of the latex would adversely affect the film morphology and hence its application as a barrier material. In view of its low glass transition temperature, natural rubber (NR) latex film is soft and tacky and cannot be used as a glove in its native form. Vulcanization and chemical modification by chlorination of the film surface are additional process steps in glove manufacturing that enable NR latex film to become finally donnable.
Basically these processes reduce the surface friction and improve the lubricity of the film surface. A clear understanding of the nature of the surface of the latex film in relation to its performance is pivotal in ensuring product quality. The adhesive force of various NR latex films such as powdered, vulcanized, chlorinated, and polymer-coated was determined from the force-distance curves using atomic force microscopy (AFM) and compared with those of synthetic polymers and commercial glove samples.
Distinctive adhesive forces between the AFM probe tip and these materials allow them to be distinguished from one another. Results indicate that the magnitude of the pull-off force is strongly influenced by surface inhomogeneity and topography of the film. The behaviour of the pull-off forces agrees with interpretation based on current understanding of this phenomenon. The technique is well-suited for assessing the structure-performance relation of gloves.

Thesis entitled

PALM OIL EMULSION FORMATION AND ITS APPLICATION TO NATURAL RUBBER LATEX DIPPED-PROCESSING

submitted by Kausar Ahmad to University of Malaya in
2002 for Ph.D degree in Chemistry.

3. List of publication

(i) C.C. Ho and M.C. Khew
"The morphology and adhesive force of natural rubber latex films by atomic force microscopy"
ACS Symposium Series 801 "Polymer Colloids" , (E.S. Daniels, E.D. Sudol, M.S. El-Aasser, ed.), American Chemical Society, Washington, DC, p239-259 (2002).

(ii) C.C. Ho, M.C. Chow
"Edible emulsions" in A. Hubbard (edi.)
"Encyclopaedia Surface and Colloid Science"
Marcel Dekker , N.Y. Vol 2, 1561-1571 (2002)

Prof. D. Horak - Academy of Sciences of the Czech Republic Institute Institute of Macromolecular Chemistry introduces itself

The Institute of Macromolecular Chemistry of the Academy of Sciences of the Czech Republic was founded in 1959 by one of the pioneers of polymer chemistry, Professor Otto Wichterle, world-wide recognized through its invention of soft contact lenses. The research activities of the Institute are aimed at the synthesis of polymers and new polymer materials, polymer physics and physical chemistry of polymers. The Institute is divided into specialized departments and groups, some of which are involved also in polymer colloid research:

Department of supramolecular polymer systems (Dr. P. Štěpánek). One of the projects deals with the study of association, complexation and micelle formation processes on microscopic, mesoscopic and macroscopic scales. Structure of core/shell micelles is characterized using diverse copolymers including polystyrene-*block*-hydrogenated polybutadiene, polystyrene-*block*-poly(methacrylic acid), polystyrene-*block*-poly(ethylene oxide), polystyrene-*block*-poly(2-vinylpyridine) (also star copolymers), poly[2-(diethylamino)ethyl methacrylate]-*block*-poly[2-(*N*-morpholino)ethyl methacrylate], poly(2-ethylhexyl acrylate)-*block*-poly(methyl methacrylate)-*block*-poly(acrylic acid), poly(2-ethylhexyl acrylate)-*block*-poly(acrylic acid) and poly(sulfobetaine)-based block copolymers (Dr. Z. Tuzar). Optical, electric and photoelectrical properties of thin polymer films are determined by static and dynamic light scattering, time-resolved light scattering, laser specle analysis, image analysis (Dr. J. Pleštil). Effect of thickeners on flow properties of acrylate latexes is studied by Newtonian and non-Newtonian viscometry; study is related to application in area of water-borne coatings or drug delivery (Dr. O. Quadrat).

Electrically conducting polymers represent a new class of polymers with many potential applications. Their processibility, however, is difficult. When their preparation is carried out in the presence of a suitable steric stabilizer, the colloidal forms are obtained and may be used, e.g., for the preparation of conducting films and coatings. Colloidal polyaniline particles of 300–400 nm size stabilized in aqueous medium with poly(1-vinyl-2-pyrrolidone) are a typical example. The collaborative IUPAC project *Conducting Polymer Colloids and Nanofilms* (http://www.iupac.org/projects/2002/2002-019-1-400.html) starting in September 2002 will be coordinated by the Institute of Macromolecular Chemistry (Dr. J. Stejskal).

Department of structure analysis (Dr. J. Kříž). Macromolecular structure and dynamics are studied on various levels starting from the atomic level (0.1 nm) up to that of supramolecular systems (100 nm) including mobility and ordering of monomer and polymer molecules building multi-layered micelles and nanoparticles of block copolymers. Monomeric methyl methacrylate was shown to be selectively sorbed in the shell of polystyrene–poly(methacrylic acid) micelles in water; its distribution and mobility were determined by NMR-PGSE techniques. The adsorbed monomer can be polymerized forming onion-like layered micelles. SANS studies of these systems are under progress. Structure of block copolymer micelles and multi-layered nanoparticles is studied using wide- and small-angle X-ray scattering.

Department of polymer network and mechanical properties (Dr. L. Matějka). Formation of polyurethane and epoxide coatings from various precursors (star, functional copolymers, hyperbranched polymers) is studied and kinetics of solvent evaporation in the organic film formation evaluated. Scratch-resistant hybrid organic–inorganic coatings are investigated and a method for determination of microhardness by AFM was developed.

Department of polymer particles (Dr. D. Horák). Projects under study include preparation of magnetic and monodisperse (monosized) particles; control of particle size, particle size distribution and porosity. Crosslinked and non-crosslinked reactive 2-hydroxyethyl and glycidyl methacrylate and 1-vinyl-2-pyrrolidone carriers with narrow size distribution and their magnetic analogs are prepared by dispersion polymerization or multi-step swelling and polymerization method. Activation of hydroxy groups by cyanuric chloride or by 4-(aminophenyl)sulfatoxyethyl sulfone and successive diazotization for azocoupling are used. Subsequently, low- and high-molecular-weight selective ligands with biospecific interactions are immobilized and the carriers used in analytical separation and catalytic processes. Similarly, bioactive compounds immobilized on magnetic and non-magnetic methacrylate and cellulose carriers find application in biochemical separation. More information on currently running studies in the Department will be described in a future Newsletter edition.

List of recently published papers

Horák D., Chaykivskyy O.: Poly(2-hydroxyethyl methacrylate-*co-N,O*-dimethacryloylhydroxylamine) particles by dispersion polymerization, J. Polym. Sci., Polym. Chem. Ed. 40, 1625-1651 (2002).

Bílková Z., Slováková M., Horák D., Lenfeld J., Churáček J.: Enzymes immobilized on magnetic carriers: efficient and selective system for protein modification, J. Chromatogr. B, Biomedical Sciences and Applications, 770, 177-181 (2002).

Matějíček P., Uhlík F., Limpouchová Z., Procházka K., Tuzar Z., Webber S. E.: Hydrophobically modified amphiphilic block copolymer micelles in non-aqueous polar solvents. Fluorometric, light scattering and computer-based Monte Carlo study, Collect. Czech. Chem. Commun. 67, 531-556 (2002).

Riede A., Helmstedt M., Sapurina I., Stejskal J.: In situ polymerized polyaniline films 4. Film formation in dispersion polymerization of aniline, J. Colloid Interface Sci. 248, 413–418 (2002).

Stejskal J., Trchová M., Prokeš J.: Poly(2-bromoaniline) and its colloidal dispersions, Collect. Czech. Chem. Commun. 67, 393–404 (2002).

Title and Abstract of a review article in press in Proceedings of Japan Academy:

When Does Like Like Like?

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Recent experimental results confirm the previous finding that ionic solute species locally form ordered structures in macroscopically homogeneous, dilute solutions. Ionic dendrimers with univalent counterions are found to show a Bragg diffraction peak in the small-angle X-ray profiles, as has been reported for other ionic polymers and colloidal particles. The Bragg spacing is smaller than the average spacing expected from concentration, suggesting the localized ordered arrangements in solutions. The localization testifies to a weak, but undeniable attraction between like-charged dendrimer ions, which is generated through the intermediary of ounterions. The *like-like* attraction is shown to disappear for bivalent counterions, however; the diffraction peak is not observed, because the charge number of the dendrimers is lowered more strongly by the bivalent ions than the univalent ones. Neutron scattering profiles for polystyrenesulfonate (PSS) solutions demonstrate diffraction peaks, sustaining the existence of the like-like attraction. The transfer from univalent counterions to bivalent ones increases the Bragg spacing, suggesting weakening of the attraction. Dynamic light scattering indicates the presence of two diffusive (fast and slow) modes for homogeneous PSS solutions, which correspond to the Brownian motion of free macroions and the motion of the localized structures, respectively. With increasing counterion valency, the fast mode becomes smaller while the slow mode is increased. A strong attraction is detected by a direct measurement of the interaction potential using colloidal particles of a high charge density while no attraction but only repulsion is found for low charge particles. This is reasonable in light of the nature of the counterion-mediated attraction. Recent computer simulation works substantiate qualitatively the existence of the like-like attraction. Quantitatively, however, they fail to reproduce the observed facts that the attraction is more intense for univalent counterions than for bivalent ones. The size of the local structure is found to depend on the diameter of filter pores employed in purification process, while the Bragg spacing is not influenced. It is concluded that the structures are ruptured by filtration and thereafter regenerated rather rapidly, suggesting that they are not filtrable aggregates but loose assemblies of macroions containing solvent. The likewise local structure is inferred to exist in simple ionic solution and in “dust” plasma as well, albeit with largely different time and length scales. The structural inhomogeneity (and hence the like-like attraction) thus appears to be one of basic features of dilute ionic systems in general.

Outline of the Monograph, "**Structure Formation in Solution - Ionic Polymers and Colloidal Particles**"

Norio Ise and I. Sogami. Contemporary Physics Series (Jiro Arafune, Hiroshi Esawa , Koichi Nakamura, Fumiko Yonezawa. Eds.), to be published by Asakura-Shoten, Tokyo. The English version is in preparation.

Chapter 1. Introduction

Ordering phenomena of ionic polymers in solutions are discussed in retrospect. The X-ray scattering study of tobacco mosaic virus particles by Bernal in 1941 triggered extensive investigation on various biopolymers, which led ones to the conclusion that the biopolymers form more or less ordered arrangement in relatively concentrated solutions. Interestingly, like Staudinger, who attributed unexpectedly high viscosity of ionic polymer solutions to the ordering of macroions in solution, Bernal suggested that the ordering was due to an electrostatic factor, namely the balance of the repulsive interaction and an attraction similar to that found in ionic crystals. Later, much more dilute regimes could be studied by new, sensitive techniques, such as neutron scattering, light scattering, small-angle X-ray scattering and ultra-small-angle X-ray scattering. A single broad peak was found by X-ray scattering for dilute solutions of various ionic polymers. Various interpretations were proposed such as an "isotropic model", "correlation hole concept" and "order formation". Accepting the third interpretation, one was led to an unanticipated conclusion that the solutions were not homogeneous in terms of solute distribution. To confirm this finding more directly, the present authors initiated concurrent microscopic study on dilute dispersions of ionic polymer latex particles, in which such an inhomogeneity in particle distributions could be "seen", albeit with time and space scales different from ionic polymer systems. To explain the inhomogeneity, the present authors claimed the presence of inter-particle or inter-macroion attraction mediated by their counterions, and discussed theoretically the interionic interaction in the framework of the Poisson-Boltzmann equation to find a long-range, electrostatic attraction. This chapter briefly describes how the experimental and theoretical advance was made.

Chapter 2. Dilute Solutions of Flexible and Spherical Polyelectrolytes

The dissociation state (the effective and analytical charge numbers) of linear and spherical polyelectrolytes such as polyacrylate and ionic dendrimers in solution is experimentally determined. The importance of counterion association phenomena is noted. The static and dynamic light scattering techniques provide a support for the structural inhomogeneity. The presence of at least two relaxation modes is confirmed. The small-angle X-ray scattering (SAXS) study reveals the "polyelectrolyte" peak, the location of which is discussed as a function of concentrations of salt and polyelectrolyte, the degree of polymerization, and temperature. It is found that the Bragg spacing from the peak is generally smaller than the average spacing from concentration, suggesting the existence of the two-state structure (polymer-rich and polymer-poor regions) in conformity with the light scattering results. The ordered structure is discussed in terms of paracrystalline distortion. The SAXS profiles of ionic micelles and ionic dendrimers are also discussed. The SAXS peak is observed for the dendrimers when the counterions are univalent while it disappears for bivalent counterions, in contrast to recent computer simulation work. Higher generations of the dendrimers give another evidence for the existence of the two-state structure. The lower effective charge numbers for the bivalent salts, which weaken the counterion-mediated attraction, are confirmed by independent conductivity measurements.

Chapter 3. Colloidal Dispersions

The experimental methods to determine directly the effective charge number of colloidal particles are first discussed. An empirical relation is derived between the analytical charge number determined by conductometric titration and the effective charge number as determined by the conductivity measurements. The purification technique of the dispersions is elaborated. The optical microscopic technique to observe the Brownian motion and the formation of colloidal crystals under low-salt condition is discussed in detail. The lattice motion, lattice plane vibration, and defects in colloidal crystals are visualized. Micrographs are shown of the two-state structure in macroscopically homogeneous dispersions. The interparticle spacing in the colloidal crystals is directly determined from micrograph or video image as a function of particle concentration, charge density, salt concentration, dielectric constant of the dispersant, and temperature. At low volume fractions, the spacing is shown to be smaller than the average spacing and is found to decrease with decreasing dielectric constant, implying that the interparticle interaction is of electrostatic nature and attractive. The micrograph showing particle distribution is Fourier-transformed to obtain the scattering profile; the radial distribution function is determined from the micrographic information. The colloidal crystal growth is followed by this technique and the Ostwald ripening mechanism is confirmed, which is in line with the existence of the attraction. The laser scanning microscope (LSM) is used to observe the inside structure of colloidal dispersion. Unexpectedly, void structures (filled with dispersant only without particles) are found below a critical particle concentration when the density of the dispersant is matched with that of the particles. It is further shown that, when the density is not adjusted, macroscopic gas-liquid phase separation occurs instead of the void formation, indicating that the void formation is a thermodynamic phenomenon. The time-resolved LSM observation shows a novel crystallization process that, immediately after the shear-melting, particles form space-filling ordered structures first, disordered regions then grow inside the ordered regions, and finally non-space-filling ordered structures are completed by accompanying shortening of the lattice constant. By the LSM observation the particle number is counted as a function of the distance from charged interfaces. In contrast with the prediction of the widely accepted double layer interaction theory, the concentration of ionic particles having the same sign as the interface or boundary decreases with increasing distance in the distance range between 5 μm and 50μm under no-salt condition. This positive adsorption is enhanced when the charge numbers of the particle and/or the interface are increased and disappears at high salt conditions. An ultra-small-angle X-ray scattering (USAXS) technique is applied to the structure study of colloidal single crystals. The crystal symmetry, lattice constant, and crystal orientation are uniquely determined. Here again the closest interparticle spacing is shown to be smaller than the average spacing at low volume fractions, while the two spacings agree at high volume fractions. Colloidal crystals can also be studied by the Kossel patterns. It turns out that the crystal properties can be more precisely determined by this technique than by scattering methods and microscopy. Furthermore, the time-resolved Kossel analysis makes clear the existence of several elementary processes in the colloidal crystal growth, which starts with highly anisotropic layer structures to end with cubic structures. The static and dynamic light scattering, dynamic X-ray scattering and neutron scattering on colloidal dispersions are also discussed.

Chapter 4. Effective Interaction in Macroionic Solutions I

In this Chapter, we review the present status of the currently accepted theoretical concepts on interionic interactions in simple electrolyte solutions and in colloidal dispersions. We limit ourselves to the mean field approach within the framework of the Poisson-Boltzmann equation. First the Debye-Hückel theory for simple salt solution is discussed in detail. Attention is drawn to the so far largely overlooked, basic problem that the electrostatic osmotic pressure is generally not negligible even in simple salt solutions so that the Helmholtz free energy (F) cannot always be equal to the Gibbs free energy (G) in ionic systems. It is mentioned that the equality of the two free energies may be assumed for weakly interacting systems such as the Debye-Hückel cases. The established Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloid stability, which is constructed by introducing the assumption of G = F, is thus limited to low charge particles. Under such an assumption, the forces between two parallel charged plates in salt solution are repulsive at the level of Helmholtz free energy. By the Derjaguin approximation, the interaction between the two particles is also purely repulsive at the level of the Helmholtz free energy. The basic feature of the error in Overbeek's criticism against the Sogami treatment is elaborated. The origin of van der Waals attraction is discussed and the nature of the Hamaker constant is elucidated.

Chapter 5. Effective Interaction in Macroionic Solutions II

Recent experimental results discussed in Chapters 2 and 3, particularly at low salt conditions, for highly charged particles and at low particle concentrations, suggest the necessity of revision of the DLVO theory. Sogami solves the *linearized* Poisson-Boltzmann equation with the assumption that the motion of the macroions is adiabatically cut off from those of the simple counterions and salt ions. The total electrostatic energy of the solution is obtained, from which the Helmholtz free energy of interaction is obtained. The Gibbs' free energy is derived therefrom. The Helmholtz pair potential results in purely repulsive interaction, in accordance with the DLVO theory, while the Gibbs pair potential leads to repulsion at small separation and attraction at large distances, creating a "secondary" minimum. In other words, the Sogami theory contains the DLVO theory as a special case. The Schultze-Hardy rule is derived also from the Sogami potential as was obtained from the DLVO theory. Without taking refuge to a van der Waals attraction as done in the DLVO theory in an *ad hoc* manner, therefore, the Sogami theory can account for the long-range attraction observed experimentally and for coagulation phenomena as well.

The mean field approach is also taken to discuss the effective interaction between highly charged plates in electrolyte solutions. Unlike in spherical systems, the Poisson-Boltzmann equation under Dirichlet and Neumann boundary conditions is solved rigorously without linearization. The *exact* solution shows that the adiabatic pair potential between the plates has a long-range weak attraction and a short-range repulsion, even at the level of the Helmholtz free energy. Most recently the Poisson-Boltzmann equation is solved without the linearization approximations to obtain the Gibbs' free energy, which showed again the existence of an electrostatic attraction between the like-charged plates, which is even stronger than that at the Helmholtz free energy level. The ubiquitous claim that the Poisson-Boltzmann approach should give only repulsion *seems* to be related to the linearization *and* the choice of the Helmholtz free energy.

Chapter 6. Viscometric Properties of Ionic Polymer Solutions and Colloidal Dispersion.

The conformation of flexible, linear polyelectrolytes is reviewed. Fuoss analysed the solution viscosity of ionic flexible polymers in terms of the Houwink - Mark -Sakurada (HMS) equation and concluded that these macroions are elongated like rods as a result of purely repulsive interaction between ionized group charges. Theoretically this equation is derived on a purely hydrodynamic consideration, and therefore its application to ionic polymer solutions, in which not only hydrodynamic but also overwhelmingly strong electrostatic interactions are involved, is not necessarily justified. Experimentally, the existence of a maximum in the viscosity-concentration curve, which was ignored in the Fuoss argument, has to be taken into consideration in determining the intrinsic viscosity. The exponent of the HMS equation after considering the maximum is not equal to 2, suggesting the inappropriateness of the rod-like model. This feature is substantiated by light scattering under low and no-salt conditions. The important role of the interaction between counterions and ionized group charges, which has been ignored in the previous argument, is stressed. This interaction generates an attraction between ionized groups through the intermediary of counterions and counteracts to the repulsive interaction between group charges. The ionic colloidal dispersions demonstrate viscometric behavior similar to the ionic polymer solutions. The viscosity-concentration curve shows also a maximum. The viscosity largely deviates from the Einstein law, particularly at low salt conditions, suggesting the overwhelmingly important role of the electrostatic interaction. An outstanding feature of the ionic system is demonstrated in the viscosity of colloidal particles and polyelectrolyte gel spheres: The viscosity decreases (not increases) with increasing charge number at a fixed particle size and also decreases with increasing size at a fixed charge density. These tendencies are not compatible with the HMS equation, and indicate that the electrostatic interaction cannot be ignored. The non-Einstein behavior at fairly large salt concentrations is successfully accounted for by Booth's theory on the first electroviscous effect, namely the distortion of the ionic atmosphere under flow.

Chapter 7. Computer Simulation and Phase Transition

The Molecular Dynamics simulation by Alder and Wainwright for hard sphere systems predicts liquid-solid transition at volume fractions of about 0.5. As mentioned in Chapters 2 and 3, the transition in ionic colloidal dispersions occurs at much lower volume fractions. This disagreement indicates inadequacy of the hard-sphere model in ionic colloidal systems. The MD simulation for particles interacting through a repulsive screened Coulomb (Yukawa) potential is used to construct the phase diagram containing a melting transition and a fcc-bcc transition. The agreement with experimental finding is not quantitatively satisfactory. The Monte Carlo (MC) and MD simulations using the Sogami potential show not only the fcc-bcc transition but also gas-liquid transition. Furthermore the void formation and the re-entrant liquid-solid-liquid transition can be reproduced by the Sogami potential but not by the DLVO potential. These results show the important role of the attractive interaction in highly charged colloidal and macroionic systems.

Chapter 8. Some other problems of the intermacroion attraction

The very general nature of the counterion-mediated attraction is stressed. The attraction originates in principle from the electric neutrality: If there were solutions containing macroions alone, the macroions naturally repel each other. However macroions without counterions are physically impossible. The coexistence of counterions with the macroions has to be admitted and then macroions attract each other through the intermediary of counterions. The most simplified case in ionic solutions is the greater stabilization of triple ions (cation-anion-cation), in which cations “attract” each other by the presence of anion inbetween, than ion pair (cation-anion) plus free cation. Such a mechanism of the attraction has been pointed out earlier in various different ways by P. Debye (joint paper with Hückel, 1923), H. Staudinger (joint paper with Trommsdorff, 1930), I Langmuir (J. Chem. Phys. 6, 873 (1938)), and R. P. Feynman (The Feynman Lecture on Physics, (1963)) It is reminded that the attraction in question is intensified and detectable only when the charge number of the macroions is high, because the macroions then more strongly interact with their counterions. In most of previous work in colloid field, in which the attraction has not been observed or could be ignored, only low charge density macroions have been employed. It is pointed out that the existing DLVO framework is valid under such conditions, while highly charged systems fall outside of this theory and show the existence of electrostatic interparticle attraction in addition to the short-range repulsion. In light of this basic nature of the attraction, the controversy on the interparticle interaction is discussed. Some colloidal properties including Schulze-Hardy rule, which have been claimed to be explainable by the DLVO theory, are demonstrated to be likewise accountable in terms of the Sogami potential. The results obtained by recently developed technique (for example, optical tweezers method) and the surface force measurements to directly determine the interparticle interaction are also scrutinized. In most of these works, though not all, satisfactory agreement with the DLVO potential is reported. However, attention is drawn to the experimental conditions adopted in these measurements (low charge density particles, high salt concentrations, and short distance from the surface), under which attraction is hardly detectable or is absent.

Reporter: D. Sunil Jayasuriya
Contribution from Johnson Polymer, 8310 16th Street, P.O. Box 902, Sturtevant, WI
53177 – 0902

Contribution #1

Patent No. 6355720
Date of Patent: March 12, 2002
Inventors: Greg M Canard, David L Trumbo and James W Taylor

ABSTRACT

Latex formulations, which exhibit a reduced amount of yellowing when exposed to heat, aldehydes or ultraviolet light contain polyfunctional amines, reducing agents, and/or reduced levels of styrene.

Contribution #2

Influence of Polymer Structure on Dry Time and Resolubility of Inks

D. Sunil Jayasuriya, Theresa R. Washkuhn, Mary Jo Biddy, Stephen A. Fischer
Johnson Polymer, Sturtevant, WI.

Presentation at the ACS National Meeting in Chicago (August 29, 2001)

ABSTRACT:

Drying and re-solubility are critical process attributes in printing water-borne inks. Rapid drying is essential to high-speed printing, and at the same time, high re-solubility is required to prevent dry ink build-up that can cause poor print quality. Ideally, rapid drying ink having good re-solubility is desired. Printing speeds are increasing and the demand for faster-drying ink without a loss in print quality is high. Although many components are added to aid drying and re-solubility in the ink system, the polymers in ink can play an important role in influencing these properties. Two water-borne polymers varying in structure, one linear and one branched, were studied. Dry rates and resolubility of the polymers and inks made from the polymers were compared. The results of this study show that a branched polymer will dry faster and is more resoluble then a linear polymer of similar composition. The studies were conducted on the neat polymer films and in an ink system. The results can be explained by the theory of polymer film formation.

Contribution #3

Surface Roughness - Gloss Study

Sunil Jayasuriya, Theresa Washkuhn, and Stephen Fischer

Presentation at the NPIRI 45th Annual Technical Conference (Oct. 17 – 19, 2001), Scottsdale, AZ

ABSTRACT

High gloss is a key property that provides visual appeal for a variety of print and coating applications. Gloss is influenced by the surface characteristics of the substrate and the physical properties of the OPV coating, which are dependent on the formation of a smooth and continuous film. Atomic Force Microscopy (AFM) was used to measure the surface roughness of various paper substrates coated with waterborne acrylic polymers. There is a strong correlation between the surface roughness and the gloss of the substrate, which can be explained by the La Mer relationship of light scattering from coalesced polymer particles.

International Polymer Colloids Group Newsletter

Haruma Kawaguchi
Faculty of Science & Technology, Keio University
Hiyoshi, Yokohama 223-8522 JAPAN

August 2002

Submitted Papers

1. **Thermo-sensitive Amphoteric Microspheres and Its Potential Application as a Biological Carrier**
   Shi-Jiang Fang and Haruma Kawaguchi
   Accepted for publication in Colloid Polym. Sci.
   Summary: Thermo-sensitive poly(N-isopropylacrylamide) (PNIPAM) moieties were introduced into amphoteric microspheres using soap-free seeded emulsion polymerization. The resulting microspheres exhibited thermo-sensitive and amphoteric behavior so that dual response to both pH and temperature was observed. This character caused unique behabior of particles to adsorb and desorb proteins.

2. **Particle Forming Precipitation Polymerization under Unusual Conditions**
   Toshio Takahashi, Hiroko Fukasawa and Haruma Kawaguchi
   Submitted to the special issue of Prog. Colloid Sci.
   Summary: Precipitation polymerization to form monodisperse PNIPAM particles were challenged in aqueous media at low temperature and successfully achieved by using co-solvent which exhibits significant co-nonsolvency effect such as ethanol. The stirring was not necessary to form particles. DMSO was another solvent to enable the formation of particles at a low temperature although the mechanism of particle formation might be different from that of ethanol/water system.

3. **Structure Characterization of Hairy Nanoparticles Consisting of Hydrophobic Core and Thermo-sensitive Hairs**
   Shinichi Takata, Mitsuru Shibayama, Reiko Sasabe and Haruma Kawaguchi
   Summary: The structure of PNIPAM hair-carrying particles in water was characterized using static and dynamic light scattering as a function of temperature. Two light scattering methods were complementary to analyze the hydrodynamic character of the hairy particles.

4. **Synthesis of Functional Polymer Particles**
   Haruma Kawaguchi
   Submitted to a monograph on “Single Organic Nanoparticles”
   Summary: A personal review in a book edited by Research project “Laser chemistry of single organic nanometer particles” supported by the Grant-in-Aid for Science Research on Priority Area, Japan. HK contributed a chapter of the preparation and functionalization of polmer particles.

5. **Thermally sensitive poly(N-isopropylacrylamide) based colloidal particles: Proteins interactions**
   H. Kawaguchi, D. Duracher, A. Elaissari
   Contributed to “Colloid Polymers: Preparation and Biomedical Applications” ed .by A. Elaissari.

6. **Dansyl Fluorescence and Local Structure of Dansyl-Labeled Core-Shell and Core-Hair Type Microspheres in Solution**
   K. Horie, S. Yamada, S. Machida, S. Takahashi, Y. Sasabe, H. Kawaguchi
   Dancyl-labeled hairy particles were prepared and the conformational state of the hair was studied by fluorescent spectroscopy.

Recent Publications

1. H. Kawaguchi, Y. Isono, S. Tsuji
   Hairy particles prepared by living radical graft-polymerization
   Macromol. Symp., 179, 75-87 (2002)
2. T. Tomohiro, J. Sawada, C. Sawa, H. Nakura, S. Yoshida, M. Kodaka, M. Hatakeyama, H. Kawaguchi, H. Handa, H. Okuno,
   Total analysis and purification of cellular proteins binding to cisplatin-damaged DNA using submicron beads
   Bioconjugate Chem., 13,163-166 (2002)
3. M. Hiramoto, N. Shimizu, M. Hatakeyama, H. Kawaguchi and H. Handa,
   High performance affinity beads for identifying anti-NF-kappa-B drug receptors
   Methods in Enzymology, 353,81-88 (2002)

Report from the Soft Condensed Matter Physics Group at the University of Surrey (UniS)
Report by J.L. Keddie

Since the publication of the Spring IPCG Newsletter, research has continued on structure and morphology of waterborne pressure-sensitive adhesives (in collaboration with UCB Chemicals, Drogenbos). In collaboration with ICI Paints, Slough, we have completed some fundamental studies of the drying of aqueous emulsions cast as films.

Published:

J. Mallégol, J.-P. Gorce, O. Dupont, C. Jeynes, P.J. McDonald, and J.L. Keddie, "Origins and Effects of a Surfactant Excess at the Surface of Waterborne Acrylic Pressure-Sensitive Adhesives," *Langmuir*, **18** (2002) pp. 4478-87.
See http://dx.doi.org/10.1021/la0117698

Accepted for Publication:

Vertical water distribution during the drying of polymer films cast from aqueous emulsions

J.-P. Gorce[1], *D. Bovey*[2], *P. J. McDonald*[1], *P. Palasz*[2], *D. Taylor*[2] *and J. L. Keddie*[1]
[1] Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH
[2] ICI Paints, Wexham Road, Slough, Berkshire SL2 5DS

We present a systematic study of the vertical uniformity of water distribution during the drying of waterborne colloidal films, testing the predictions of a Peclet number *Pe* defined for this system. *Pe* indicates the relative contributions of water evaporation and Brownian diffusion in determining the concentration profile in the vertical direction (*i.e.* normal to the substrate). When $Pe < 1$, the water concentration in films cast from an alkyd emulsion is found via magnetic resonance profiling to be uniform with depth, which is consistent with expectations. When $Pe > 1$, a gradient in the water concentration develops, with less water near the interface with air. The water profiles reveal that the alkyd particles do not coalesce immediately upon contact in close-packing. At later times, a concentrated surface layer develops, but particles are not coalesced in this layer to form a continuous "skin", but rather the structure is likely to be that of a biliquid foam.

(To appear in *European Physical Journal E*)

Inhibition of the Surface Levelling of Thermosetting Polyester Powder Coatings Caused by Surface Tension Gradients

Y. Zhao,[1] J.D. Carey,[1] N. Knoops,[2] D. Maetens,[2] I. Hopkinson,[3] J.N. Hay[1] and J.L. Keddie[1]

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Previous theoretical and experimental work has shown that surface tension gradients in liquid layers create surface defects and inhibit the levelling of an uneven surface. In coatings deposited from thermosetting polyester powders, which are studied here, small amounts of a low molecular-weight acrylate are incorporated to act as a "flow agent". We find that this additive lowers the surface tension of the polymer melt and has a minor effect on the melt viscosity. A slower rate of levelling results from the decreased surface tension. We provide experimental evidence that lateral gradients in the surface tension of the polymer melt, resulting from the non-uniform distribution of the flow agent, inhibit the levelling of the surface. Specifically, the surface roughness of a powder coating is up to three times greater when a steep surface tension gradient is purposely created through powder blending. Surface tension gradients might also be responsible for the greater surface roughness (observed with atomic force microscopy on lateral length scales of 100 μm) that is found in coatings that contain flow agent.

(To appear in *Journal of Materials Science*)

Submitted for Publication:

Morphology and Elasticity of Waterborne Acrylic Pressure-Sensitive Adhesives Investigated with Atomic Force Microscopy

J. Mallégol,[1] O. Dupont[2] and J.L. Keddie[1]

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2. UCB Chemicals, 33 Anderlechtstraat, Drogenbos B1620, Belgium

The morphology of pressure sensitive adhesives (PSAs), especially at the surface in contact with the release liner, is expected to have a dominant influence on the tack strength and energy. We have used tapping-mode atomic force microscopy to determine the morphology at the surfaces of freshly-cast waterborne acrylic PSAs over lateral length scales of a few μms. We demonstrate that topographical features on silicone release liners can be used to pattern the PSA surface in contact with it. Control of the texture of a PSA surface can potentially be exploited to tailor its properties. Particle boundaries are much better defined at the air surface of the PSA in comparison to its back face. A series of experiments suggest that this difference results from the distribution of water-soluble species within the dry film. The pressures and surfaces involved in the transfer lamination process do not alter the PSA morphology. The first reported AFM images of the response of these materials to pressure and shear provide insight into the deformation mechanisms. Amplitude-distance curves on PSA surfaces show that there is very change in tack or stiffness after ageing for 13 months.

(Submitted to *Journal of Adhesion Science and Technology*)

Up-to-date information on all publications of J.L. Keddie can be found at
http://www.ph.surrey.ac.uk/polcol/publications.htm

Using Dispersion/Flocculation Phase Diagrams to Visualize Interactions of Associative Polymers, Latexes, and Surfactants

E.C. Kostansek
Rohm and Haas Company

The colloidal interactions of associative polymers and latexes in the presence of surfactant is complex. This is because, in addition to good particle dispersion, both bridging and depletion flocculation can occur. Therefore, we have developed dispersion/flocculation phase diagrams to help visualize these interactions. The various phases have a significant effect on coatings and applications properties including rheological, optical and resistance properties. We present here examples of experimentally determined phase diagrams for a model HEUR nonionic associative polymer and various latexes in the presence of sodium dodecylsulfate. A 140 – 600 nm particle size range for both hydrophilic and hydrophobic latexes was explored. The major variables affecting phase behavior were found to be associative polymer concentration, latex particle size, latex surface hydrophobicity, and electrolyte, cosolvent, and surfactant concentrations.

Controlled Coagulation of Emulsion Polymers

E.C. Kostansek
Rohm and Haas Company

Coagulation of submicron latex emulsion particles is most often carried out in the diffusion limited aggregation (DLA) regime where coagulation rates are very high and the time for coagulation to take place is on the millisecond timescale. This process produces aggregates of low density, irregular shape, and a broad particle size distribution. When the coagulation is carried out in the reaction limited aggregation (RLA) regime, a coagulation time of about 1 – 100 sec., the system can be controlled to yield dense, spheroidal aggregates with a very narrow particle size distribution. This phenomenon usually occurs in the region between 5% and 20% volume solids and is quite unexpected and unique. Below 5 % solids there is incomplete coalescence and above 20% solids the viscosity during coagulation becomes prohibitively high. When the aggregates are dried, the powder derived from RLA has much better mechanical and flow properties than the powder derived from DLA. This paper discusses the effects of polymer composition, latex particle size, temperature, and vessel agitation on the formation of RLA aggregates. The kinetics of the coagulation process is described in terms of colloid theory and the DLVO model. Micrographs will be shown illustrating the surprisingly uniform and dense aggregates which can be achieved by performing a carefully controlled RLA process. The practical applications of controlled coagulation will also be discussed.

Contribution to IPCG newsletter from the

Leiden Colloid and Interface Science group
and the Laboratory of Physical Chemistry, Delft University of Technology

A complete list of published material is available on
http://www.dct.tudelft.nl/lfc/persons/gkoper/Publ.htm

Relevant recent publications

- Haemers S, Koper GJM, van der Leeden MC, Frens G: **An alternative method to quantify surface plasmon resonance measurements of adsorption on flat surfaces**. *LANGMUIR* 2002, **18:**2069-2074.
- Chassagne C, Bedeaux D, Koper GJM: **Dielectric enhancement of charged nanospheres dispersed in an electrolyte**. *J PHYS CHEM B* 2001, **105:**11743-11753.
- Mezzasalma SA, Koper GJM: **Semiclassical approach to electrorheological fluids. Influence of solid volume fraction on the suspension yield stress**. *COLLOID POLYM SCI* 2002, **280:**160-166.
- Shchipunov YA, Mezzasalma SA, Koper GJM, Hoffmann H: **Lecithin organogel with new rheological and scaling behavior**. *J PHYS CHEM B* 2001, **105:**10484-10488.
- Haemers S, van der Leeden MC, Koper GJM, Frens G: **Cross-linking and multilayer adsorption of mussel adhesive proteins**. *LANGMUIR* 2002, **18:**4903-4907.

Relevant preprints:

Film formation from concentrated emulsions studied by simultaneous conductometry and gravimetry

F. Bouchama, G. Estramil, A. J. E. Autin, and G. J. M. Koper

We present a simple, yet effective, technique involving simultaneous conductometry and gravimetry, to study the drying process of films made from concentrated oil-in-water emulsions. We exemplify the technique by drying experiments on paraffin oil/Triton X100/brine emulsion films.

The drying process is demonstrated to consist of three regimes: (1) evaporation of “free water", (2) dehydration of the bi-liquid (o/w) foam, and (3) the rupture of the foam structure into an inverted (w/o) emulsion. Conclusive statements about the morphology of the emulsion film in each of these stages are made, based on observations using the above technique.

Synthesis and Protonation Behavior of Comb-Like Poly(Ethylene Imine)

Ger J.M. Koper, René C. van Duijvenbode, Danny D.P.W. Stam, Michal Borkovec

Comb-like poly(ethylene imine) (PEI) with -(CH_2CH_2N)($CH_2CH_2NH_2$)- as the repeating unit has been synthesized employing a protecting group strategy, and analyzed by potentiometric titration. Plotted the degree of protonation as a function of pH, the titration curve shows three protonation steps separated by two intermediate plateaus, namely one at degree of protonation of 1/2 and a second one at 3/4. The first protonation step occurring at pH around 9.5 corresponds to the protonation of the primary amine groups on the side chains. During the second protonation step at pH around 4.5 every second tertiary amine protonates, while the final protonation step, where the remaining tertiary amines protonate, probably occurs at pH near 0. The titration curve can be quantitatively predicted to a good degree of accuracy using a site binding model, which has been independently calibrated on titration data of low weight molecular amines.

Dielectric Spectroscopy Measurements on Latex Dispersions

C. Chassagne, D. Bedeaux, J.P.M v.d. Ploeg, and G.J.M. Koper

Experimental data on the dielectric response of latex dispersions for a large variety of particle sizes, surface charge densities and ionic strengths are interpreted using an analytical theory developed previously
(Chassagne, C., Bedeaux, D. and Koper, G.J.M., J.Phys.Chem B **105**, 11743 (2001) and Physica A, to be published). It is found that the conductivity increment is a crucial variable in the discussion about the need of a Stern layer conductance. Both the dielectric permittivity and the conductivitty increments are fitted using the zeta potential and a Stern layer conductance.

Theory of Electrode Polarization. Application to Parallel Plate Cell Dielectric Spectroscopy Experiments

C. Chassagne, D. Bedeaux, J.P.M. van der Ploeg, and G.J.M. Koper

An extension of the model for electrode polarization of Cirkel (Cirkel P.A.; v.d. Ploeg J.P.M.; Koper G.J.M., Physica A **235**, 269 (1997)) is given. The problem is solved using both classical boundary conditions and the new boundary conditions using excess densities presented in a previous paper (Chassagne C.; Bedeaux D.; Koper G.J.M., J. Phys. Chem. B , **105**, 11743 (2001)). In the present paper, the electrodes are supposed to be ideal, meaning that charge transfer or adsorption are not considered. The advantage of the new boundary conditions lies in the possibility to extend to more complicated situations including for instance specific ion adsorption. We prove that the new boundary conditions and classical ones give the same results. A comparison of the model predictions, involving no adjustable parameters, experimental dielectric spectroscopy data is performed and fairly good agreement is found.

Polarization between Concentric Cylindrical Electrodes

C. Chassagne, D. Bedeaux, J.P.M v.d. Ploeg, and G.J.M. Koper

We consider an asymmetric electrolyte between two cylindrical concentric electrodes that are uncharged in the absence of an applied voltage difference. We calculate the dielectric response of this capacitor to an alternating voltage difference. The problem is solved using both classical boundary conditions and the new boundary conditions using excess densities to describe the charge build-up near the condensator plates as given in a previous article (C. Chassagne, D. Bedeaux and G.J.M. Koper , Colloid and Surfaces A}). We verify that both boundary conditions give the same results. The advantage of the new boundary conditions lies in the possibility to extend, in the future, the analysis to real electrodes including reactions and specific ion adsorption. A comparison of the model predictions, involving no adjustable parameters, with experimental dielectric spectroscopy data is performed and excellent agreement is found.

REPORT FROM HANS LYKLEMA, WAGENINGEN, NL

Over the past months I have been mostly active in the domains of electrokinetics and colloid stability, the latter in connection with the writing of Volume IV of my series 'Fundamentals of Colloid and Interface Science', entitled 'Pair Interactions'

Publications include the following.

J.Lyklema, Colloids Surf.A186 (2001)11. A discussion on surface entropies.

J.Lyklema, J.Phys. Condens. Matter, 13 (2001). 5027. 'Surface Conduction'

J.Lyklema, 'The Role of Surface Conduction in the evelopment of Electrokinetics' in 'Interfacial Electrokinetics and Electrophoresis' A.V. Delgado, Ed., Marcel Dekker 2002, 87

J.Duval, J.Lyklema. H.P.van Leeuwen and J.M. Klein, Langmuir 17 (2001) 7573. Amphifunctionally Electrified Interfaces: Coupling of Electronic and Ionic Charging Processes'

M.Löbbus, J.Sonnefeld, H.P.van Leeuwen,W.Vogelsberger and J.Lyklema, 'ESA measurements for Surface Characterization. An Improved Method to Calculate Zeta-potentials' in Encyclopaedia of Surface and Colloid Science, A.M. Hubbard, Ed, (2002).1864

Contribution to Polymer Colloids Group Newsletter

M. Nomura, H. Tobita and K. Suzuki
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News on Polymer Colloids in Japan:

The 12th Polymeric Microspheres Symposium (domestic) is to be held in Fukui University in November 6-8, 2002 with 73 papers presented. The preprints, although the text is written in Japanese, but most Figures are presented in English, is available at free of charge by direct request to M. Nomura. The titles of the papers presented will be introduced in the next IPCG Newsletter.

Recent Research Activity on Polymer Colloids in Fukui University:

(1) Emulsion Copolymerization of Vinylidene Chloride and Methyl Methacrylate. I. Effects of Operating Variables on the Kinetic Behavior
M. Nomura, H. Sakai, Y. Kihara, and K. Fujita, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 1275-1284 (2002)

(2) Film-Formation Property of Vinylidene Chloride-Methyl Methacrylate Copolymer Latex. I. Effect of Emulsion Polymerization Process
H.Sakai, T. Kodani, A. Takayama, and M. Nomura, *J. Polym. Sci., Part B: Polym. Phys.*, **40**, 939-947 (2002)

(3) Kinetics and Mechanism of O/W Microemulsion Polymerization of Styrene
K. Suzuki and M. Nomura, *Macromol. Symp.*, **179**, 1-12 (2002)

(3) Film-Formation Property of Vinylidene Chloride-Methyl Methacrylate Copolymer Latex. II. Effect of Latex Strage Temperature
H.Sakai, T. Kodani, A. Takayama, and M. Nomura, *J. Polym. Sci., Part B: Polym. Phys.*, **40**, 948-9953 (2002)

(4) Determination of Propagation Rate-Constant of Vinylidene Chloride by Emulsion Polymerization
H. Sakai, Y. Kihara, K. Fujita, and M. Nomura, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 1005-1015 (2001)

(5) Continuous Emulsion Polymerization of Styrene in a Single Couette-Taylor Vortex Flow Reactor
X. wei, H. Takahashi, S. Sato, and M. Nomura, *J. Appl. Polym. Sci.,* **80**,1931-1942 (2001)

(6) Continuous Emulsion Polymerization of Vinyl Acetate I. Operation in a Continuous Stirred Tank Reactor Using Sodium Lauryl sulfate as Emulsifier
M. Nomura et al., *J. Appl. Polym. Sci.,* in printing

(7) Continuous Emulsion Polymerization of Vinyl Acetate II. Operation in a Single Couette-Taylor Vortex Flow Reactor Using Sodium Lauryl sulfate as Emulsifier
M. Nomura et al., *J. Appl. Polym. Sci.,* in printing

<Publications 2002>

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1. Structural conformation of biomolecules desorbed from temperature-sensitive composite polymer particles a study by CD

H. Ahmad, M. Okubo, Y. Kamatari, H. Minami , *Colloid Polym. Sci.*, **280** (4), 310-315 (2002)

A conformational study of the biomolecules desorbed from 0.184 µm- and 1.8 µm-sized temperature-sensitive composite polymer particles by descending the temperature from 40˚C to 25˚C was estimated with circular dichroism in comparison with those of the native ones. In almost all cases the desorbed biomolecules retained their native conformational states.

2. Formation mechanism of multihollow structure within submicron-sized styrene-methacrylic acid copolymer particles by the alkali/acid method

M. Okubo, A. Sakauchi, M. Okada, *Colloid Polym. Sci.*, **280** (4), 303-309 (2002)

The formation mechanism of multihollow structure within submicron-sized styrene-methacrylic acid copolymer particles by the stepwise alkali/acid method, which we had proposed in 1990, was discussed thermodynamically from the viewpoint of interfacial free energy.

3. Morphology of Micron-Sized, Monodisperse, Nonspherical Polystyrene/Poly(n-butyl methacrylate) Composite Particles Produced by Seeded Dispersion Polymerization

M. Okubo, T. Miya, H. Minami, R. Takekoh, *J. Appl. Polym. Sci.*, **83** (9), 2013-2021 (2002)

Nonspherical polystyrene (PS)/poly(n-butyl methacrylate) (PBMA) composite particles with uneven surfaces were produced by seeded dispersion polymerization of BMA with 1.65-m, monodisperse, spherical PS seed particles. The composite particles consisted of a PS core and an incomplete PBMA shell. The formation mechanism of such nonspherical particles was discussed.

4. Evaporation behavior of water from aqueou dispersion of multihollow polymer particles prepared by the stepwise alkali/acid method

M. Okubo, A. Sakauchi, M. Okada, *Colloid Polym. Sci.*, **280** (1), 38-45 (2002)

In order to clarify the formation mechanism of multihollow structure inside styrene-methacrylic acid copolymer particles prepared by the stepwise alkali/acid method, which we proposed in 1990, evaporation behavior of water from aqueous dispersions of the original carboxylated particles and those after the alkali treatment and the stepwise alkali/acid treatments was examined. It is concluded that the particle after the alkali treatment had a number of small-sized water pools in the inside.

5. Production of submicron-sized poly(methyl methacrylate) particles by dispersion polymerization with a poly(dimethylsiloxane)-based azoinitiator in supercritical carbon dioxide

M. Okubo, S. Fujii, H. Maenaka, H. Minami, *Colloid Polym. Sci.*, **280** (2), 183-187 (2002)

Submicron-sized, comparatively monodisperse poly(methyl methacrylate) particles were produced by dispersion polymerization of methyl methacrylate with poly(dimethylsiloxane)-based azoinitiator in supercritical carbon dioxide at 30 MPa for 24 h at 65˚C. The initiator operated as not only radical initiator but also colloidal stabilizer, which was named “ini stab”.

6. Variation of morphology of carboxylated polymer film by alkali treatment

M. Okubo, M. Okada, A. Ito, T. Suzuki, *Colloid Polym. Sci.*, **280** (6), 574-578 (2002)

Variation of the morphology of styrene-methacrylic acid copolymer film cast from tetrahydrofuran solution before and after alkali treatment was observed with a scanning electron microscope. The copolymer was synthesized by emulsion copolymerization. The treated film had a porous structure. This result gives an important proof for the formation mechanism of the multihollow structure in submicron-sized, carboxylated polymer emulsion particles by the stepwise alkali/acid method and the alkali/cooling method which the authors proposed.

7. Preparation of nonspherical particles by spraying aqueous dispersion of hydrophobic solvent droplets dissolving various polymers into methanol

M. Okubo, Y. Konishi, S. Salim, H. Minami, *Colloid Polym. Sci.*, **280** (8), 765-769 (2002)

Nonspherical polymer particles were prepared by spraying an aqueous dispersion of hydrophobic solvent droplets dissolving various polymers into methanol. Nonspherical particles were prepared for polystyrene and poly(methyl methacrylate), meanwhile spherical ones were prepared for the case of poly(ethyl methacrylate) and poly(i-butyl methacrylate). It is concluded that condensation of the polymer molecules at the interface of the droplet is a key factor for the formation of nonspherical polymer particle.

8. Heterogenity among multihollow polymer particles prepared by the alkali/cooling method under partial neutralization conditions

M. Okubo, M. Okada, K. Shiba, *Colloid Polym. Sci.*, **280** (9), 822-827 (2002)

Heterogeneity in the formation of multihollow structure among styrene-methacrylic acid copolymer particles, which were produced by emulsion copolymeriization, by alkali/cooling method under partial neutralization conditions with potassium hydroxide was investigated. There was a threshold acid content to form the multihollow structure. The heterogenity among the multihollow particles was based on the heterogeneity of acid content among the original particles.

Contribution to the IPCG Newsletter July 29, 2002

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Main activities of our group are on colloidal crystals, their morphology, crystal structure, crystal growth kinetics and effect of external fields such as a gravitational field, an electric field, and a centrifugal field. Microgravity effect on colloidal dispersions has been studied systematically using dropping, aircraft and rocket techniques. Dissipative structures of colloidal dispersions, alternate multi-layered complexation of colloidal spheres with macroions, and seed polymerization of TEOS are also included in our recent research fields.

Publications (2002-)

Colloidal Crystals and Colloidal Liquids

(1)"**Rheological Properties of Sodium Montmorillonite in Exhaustively Deionized Dispersions and in the Presence of Sodium Chloride**", H. Kimura and T. Okubo, *Colloid Polymer Sci.*, **280**, 579-583 (2002).

(2)"**Kinetics Analysis of Colloidal Crystallization of Silica Spheres Modified with Polymers on Their Surfaces in Acetonitrile**", T. Okubo, H. Ishiki, H. Kimura, M. Chiyoda and K. Yoshinaga, *Colloid Polymer Sci.*, **280**, 290-295 (2002).

(3)"**Colloidal Crystallization of Monodisperse and Polymer-Modified Colloidal Silica in Organic Solvents**", K. Yoshinaga, M. Chiyoda, H. Ishiki and T. Okubo, *Colloid Surfaces*, **A204**, 285-293 (2002).

(4)"**Crystalline Colloids**", T. Okubo, *Encycopedia Surf. Colloid Sci.*, A. Hubbard(ed), Marcel Kekker, pp1300-1309 (2002).

(5)"**Structural and Dynamic Properties of Colloidal Liquids and Gases of Silica Spheres (29 nm in Diameter) As Studied by the Light Scattering Measurements**", T. Okubo and A. Tsuchida, *Colloid Polymer Sci.*, **280**, 438-445 (2002).

(6)"**Rigidity of Colloidal Crystals of Silica Spheres Modified with Polymers on Their Surfaces in Organic Solvents**", T. Okubo, H. Ishiki, H. Kimura, M. Chiyoda and K. Yoshinaga, *Colloid Polymer Sci.*, **280**, 446-453 (2002).

(7)"**Rheo-optical Study of Colloidal Crystals**", T. Okubo, H. Kimura, T. Hatta and T. Kawai, *Phys.Chem.Chem.Phys.*, **4**, 2260-2263 (2002).

(8)”**Rigidity of Colloidal Crystals of Silica Spheres Modified with Polymers on Their Surfaces in Organic Solvents**”, T. Okubo, H. Ishiki, H. Kimura, M. Chiyoda and K. Yoshinaga, *Colloid Polymer Sci*., **280**, 446-453 (2002).

(9)”**Electro-optics of Colloidal Crystals Studied by the Electric Potential and Reflection Spectroscopy**”, A. Tsuchida, M. Kuzawa and T. Okubo, *Colloid Surfaces*, in press.

(10)”**Thermo-Sensitive Colloidal Crystals of Silica Spheres in the Presence of Gel Spheres of Poly(N-isopropyl acrylamide)**”, T. Okubo, H. Hase, H. Kimura and E. Kokufuta, *Langmuir*, in press.

Microgravity Experiments

(11)”**Rotational Diffusion of Tungstic Acid Colloids in Microgravity as Studied by Aircraft Experiments**”, T. Okubo, A. Tsuchida, H. Yoshimi, K. Taguchi and S. Kiriyama, *Colloid Polymer Sci.*, **280**, 228-233 (2002).

(12)”**Microgravity Effects on Some Thermodynamic and Kinetic Properties of Colloidal Dispersions**”, T. Okubo and A. Tsuchida, Microgravity Transport Processes in Fluid, Thermal, Biological and Material Sciences, S. S. Sadhal(ed), *Ann. New York Acad. Sci*., in press.

Dissipative Structures

(13)”**Dissipative Structures Formed in the Course of Drying the Colloidal Crystals of Silica Spheres on a Cover Glass**”, T. Okubo, S. Okuda and H. Kimura, *Colloid Polymer Sci.*, **280**, 454-460 (2002).

Colloid-Macroion Complexation

(14)”**Synchronous Multi-layered Adsorption of Macrocations and Macroanions on Colloidal Spheres. Influence of Foreign Salt and Basicity or Acidity of the Macroions**”, T. Okubo and M. Suda, *Colloid Polymer Sci.*, **280**, 533-538 (2002).

Contribution to IPCG Newsletter From Laboratoire de Chimie des Procédés de Polymérisation(LCPP-CNRS)
and Unité Mixte CNRS-bioMérieux
Lyon-France

(submitted by E. Bourgeat-Lami, A. Elaïssari, C. Pichot)

REVIEW

JOURNAL OF NANOSCIENCE AND NANOTECHNOLOGY, **2**, 1-24 (2002)

Organic–Inorganic Nanostructured Colloids

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The synthesis and applications of organic–inorganic nanostructured colloids and colloidal-based materials are reviewed here. Emphasis is placed on the strategies and synthetic methods developed to organize organic–inorganic architectures. The article begins with a description and a general hierarchical classification of different systems, from inorganic particle synthesis and surface modification to more elaborate nanostructured colloids obtained through *in situ* encapsulation and/or self-assembly techniques. Ordering of colloids into two- and three- dimensional arrays and their use as templates is also considered. For every system, typical examples are given that highlight the advantages and limitations of the techniques, as are more recent developments. Some properties and applicability of organic–inorganic colloids in catalysis, medicine, and coating technologies are also cited.

Keywords: Nanostructured, Colloid, Organic, Inorganic, Grafting, Encapsulation, Heterophase Polymerization, Self-assembly.

ARTICLES

Synthesis and Characterization of SiOH-Functionalized Polymer Latexes Using Methacryloxy Propyl Trimethoxysilane in Emulsion Polymerization

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ABSTRACT: Polystyrene latex particles carrying silanol groups on their surface have been synthesized in emulsion polymerization using 3-(trimethoxysilyl)propyl methacrylate (MPS) as a functional comonomer. We showed that the colloidal stability of the resulting latex suspensions was highly dependent on pH and on the nature of the surfactant. The structure of the hybrid copolymers was analyzed using infrared and solid-state NMR spectroscopies. Condensation reactions of the silane molecule were promoted at high and low pH and were also influenced by the silane content in the monomer mixture. No condensation products were formed when polymerization was performed at pH 7 using 10 wt % MPS (relative to styrene*)* indicating that it is possible to control the cross-linking process under these conditions. The functionalization reaction was extended further to poly(methyl methacrylate) and poly(butyl acrylate) latexes. In contrast to polystyrene, condensation products were identified in both cases presumably because of difference in comonomers reactivity ratios, and perhaps also because of difference in molecular mobility. Independent of the microstructure of the hybrid copolymers, AUGER electron spectroscopy and electrophoretic measurements gave evidence of the presence of silanol groups on the particle surface. The SiOH functionality is of great interest in applications where it can be necessary to control the surface properties of polymer colloids. The hybrid copolymers provide rigidity to the surface and can significantly influence mechanical properties of the material. In addition, the SiOH groups can be efficient primers for the subsequent growth of a mineral layer around the particles and can help compatibilize organic colloids with inorganic materials in nanocomposite structures or higher hierarchical devices.

Macromol. 2002, 35, 6185-6191.

Synthesis and Characterization of Silica/Poly (Methyl methacrylate) Nanocomposite Latex Particles through Emulsion Polymerization Using a Cationic Azo Initiator

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Received November 2, 2001; accepted February 21, 2002; published online April 29, 2002

ABSTRACT : Following a previous work (J. L. Luna-Xavier *et al.*, *Colloid Polym. Sci.* **27**9, 947 (2001)), silica–poly (methyl methacrylate) (PMMA) nanocomposite latex particles have been synthesized in emulsion polymerization using a cationic initiator, 2,2-azobis (isobutyramidine) dihydrochloride (AIBA), and a nonionic polyoxyethylenic surfactant (NP30). Silica beads with diameters of 68, 230, and 340 nm, respectively, were used as the seed. Coating of the silica particles with PMMA was taking place *in situ* during polymerization, resulting in the formation of colloidal nanocomposites with a raspberry-like or a core–shell morphology, depending on the size and nature of the silica beads. The amount of surface polymer was quantified by means of ultracentrifugation and thermogravimetric analysis as extensively described in the first article of the series (see above reference). The influence of some determinant parameters such as the pH of the suspension, the initiator, silica, monomer, or surfactant concentration on the amount of coating polymer and on the efficiency of the coating reaction was investigated in details and discussed in light of the physicochemical properties of the seed mineral. Electrostatic attraction between the positive end groups of the macromolecules and the inorganic surface proved to be the driving force of the polymer assembly on the seed surface at high pH, while polymerization in adsorbed surfactant bilayers (so-called admicellar polymerization) appeared to be the predominant mechanism of coating at lower pH. Optimal conditions have been found to reach high encapsulation efficiencies and to obtain a regular polymer layer around silica.

Key Words: emulsion polymerization; heterocoagulation; nanocomposite; colloidal silica; cationic initiator; polyoxyethylenic surfactant.

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Syntheses of Raspberry-like Silica/Polystyrene Materials

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ABSTRACT : Raspberry-like hybrid organic-inorganic materials consisting of spherical silica beads supporting smaller polystyrene particles were prepared through a heterophase polymerization process. In a first step, micrometer-sized silica particles were synthesized according to procedures inspired from the literature. In a second step, a poly(ethylene glycol) macromonomer was adsorbed on the surface of the silica beads. Finally, polymerization of styrene was achieved in water with a nonionic surfactant as an emulsifying agent and sodium persulfate as an initiator. Scanning and transmission electron microscopies show that the presence of the macromonomer on the surface of the silica particles is a determining parameter in order to get the raspberry-like morphology.

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Encapsulation of an Organic Phthalocyanine Blue Pigment into Polystyrene Latex Particles using a Miniemulsion Polymerization Process

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ABSTRACT : Aqueous dispersions of polystyrene latexes encapsulating a copper phthalocyanine blue pigment were formulated using the miniemulsion polymerization technique. The organic pigment was first suspended into the monomer phase, and the resulting oily suspension was subsequently converted into stable miniemulsion droplets using various types and concentrations of hydrophobe (costabilizer). The pigmented monomer emulsions were finally polymerized using potassium persulfate as the initiator. It was shown that the organic pigment could stabilize the miniemulsion droplets, and be thus satisfactorily encapsulated without introducing any other compound in the formulation. In a subsequent approach, the stability of the miniemulsion droplets was improved by using either hexadecane, hexadecanol or a polystyrene prepolymer as the hydrophobe. Dynamic light scattering and transmission electron microscopy measurements showed that the size and the morphology of the resulting pigmented polymer particles were greatly influenced by the presence of the costabilizer.

Keywords: encapsulation, phthalocyanine, organic pigment, miniemulsion, polymerization

Polym. Int. **2002,** *51,* 1-7

Poly(D,L-lactic acid) nanoparticle preparation and colloidal characterization

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Abstract: Nano size-ranged poly(D, L-lactic acid) (PLA) particles were obtained from 2-10 w% PLA solution in water saturated Ethyl Acetate by the emulsification-diffusion method. The main factor affecting the particle size was the PLA solution concentration. Pluronic F68 used in the formulation was shown to adsorbed at the interface at 0.5 mg/m^2, irrespective of the initial surfactant concentration and particle size. The molecular occupied area of 24 nm^2/molecule suggested an expanded conformation of the surfactant at the interface, though an incomplete coverage can not be excluded. Coagulation kinetics measurements revealed a Critical Coagulation Concentration (CCC) of 1.4 M indicating a steric stabilization of the colloids by the adsorbed triblock copolymer. Nevertherless, variations in zeta potential with increasing salt concentration were observed suggesting that the surface carboxylate groups were still accessible for further modifications.

Key words : nanoparticles – emulsification-diffusion – surface charge - colloidal stability.

Surface functionalization of poly(D,L-lactic acid) nanoparticles with poly(ethylenimine) and plasmid DNA by the Layer-by-Layer approach.

T. Trimaille, C. Pichot, T. Delair*

Abstract
The layer-by-layer approach was used for the elaboration of nanosized DNA carriers. Poly (D, L lactic acid) (PLA) particles obtained by the emulsification-diffusion process were surface modified by electrostatic interactions with cationic poly(ethylenimine) (PEI). The charge inversion was evidenced by zeta-potential measurements and the adsorption isotherms of PEI were established. The mean diameter of the cationized particles were measured by Quasi Elastic Light Scattering (QELS) and visualized by Scanning Electron Microscopy (SEM). No flocculation was observed so long as the PEI amount in the adsorption medium was close the surface saturation. The amount of

immobilized PEI was affected by the ionic strength of the medium. In the absence of salt, lower loading levels were achieved and the modified colloids displayed a quasi-neutral zeta-potential, due to the charge-to-charge neutralization. Hence, a flat conformation of the polymer was deduced. When salt was added to the adsorption medium, higher amounts of polymer were immobilized at the surface of the PLA particles. Moreover, the colloids were highly positively charged (+ 20-30 mV), which suggested a loops and tails conformation of the PEI at the inteface. Onto the cationized PLA particles, a model plasmid was adsorbed. The two main parameters controlling this step were the pH of the adsorption medium and the interfacial conformation of the polycation. With a decrease in pH, resulting in the reduction of the surface potential of the particles, the DNA was less efficiently attracted by the colloidal carrier. Hence, lower saturation levels were observed.When the PEI was adsorbed flat at the interface, low amounts of plasmid were adsorbed and a poor compaction of the DNA molecules was observed by the Ethidium Bromide displacement method. With the highly positively charged particles obtained by adsorption of PEI in thepresence of salt, the amounts of immobilized DNA were higher than in the previous conditions and, moreover, the compaction of the plasmid on forming polyelectrolyte complexes with the particles was as efficient as with the free PEI in solution.

Key words: Poly(D,L lactic acid); Layer-by-Layer; plasmid DNA, isotherms; poly(ethylenimine)

Surface functionalization of oil-in-water nanoemulsion with a reactive copolymer: colloidal characterization and peptide immobilization

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Abstract

Cationic oil-in-water emulsion droplets were prepared using medium chain triglycerides (MCT), phosphatidylcholine / phosphatidylethanolamine phospholipid mixtures (Lipid E-80), Pluronic F68 and poly[*N*-acryloylmorpholine-*co*-*N*-acryloxysuccinimide] (poly[NAM/NAS]) copolymer functionalized with N-(acetyl)spermine and decylamine through chemical reaction with succinimide groups. In addition, 2-(2-pyridyldithio)ethylamine was grafted onto copolymer in order to target the covalent binding of a peptide model. At first, the obtained emulsion was characterized by quasi-elastic light scattering analysis revealing an average droplet diameter around 200 nm and a relatively narrow droplet size distribution. Electrokinetic study and colloidal stability were also performed as a function of both pH and salinity, showing the marginal effect of the Pluronic used as stabilizing agent and confirming the presence of the functionalized copolymer at the interface. Secondly, the immobilization of Influenza hemagglutinin HA-2 derived peptide was carried out on the droplet surface and highlighted the contribution of covalent binding onto the functionalized copolymer to the fixation process.

Polymer mediated peptide immobilization onto amino-containing N-isopropylacrylamide -styrene core-shell particles

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Abstract

Monodisperse cationic core-shell latex particles have been prepared using a shot polymerization process, with N-(3-aminopropyl)-methacrylamide) hydrochloride (APMH) as the functional monomer. The final latexes were characterized with respect to final polymerization conversion, water soluble polymer formation, particle size and size distribution, surface charge density and electrokinetic properties. Then, the covalent grafting of maleic anhydride-alt-methyl vinyl ether (MAMVE) copolymer onto aminated latex particles was investigated. The most efficient conditions to obtain derivatized particles with no alteration of the colloidal stability were to control both polymer amount/latex particles concentration ratio and the mixing methodology of both species. The charge inversion of the hydrolyzed MAMVE functionalized particles was evidenced by measuring the electrophoretic mobility as a function of pH. Finally, the covalent binding approach was implemented with peptide-MAMVE conjugates, confirming the great potential of this promising methodology for elaborating reactive latex particles bearing peptides.

Key words: temperature sensitive, core-shell latex, reactive copolymer, covalent coupling, peptides

Adsorption of Bovine Serum Albumin Protein onto Amino-containing Thermosensitive Core-shell Latexes

David Duracher, Raphaël Veyret, Abdelhamid Elaïssari*, Christian Pichot

Abstract: Adsorption of bovine serum albumin (BSA) onto positively charged core-shell latex particles with a poly(styrene) core and a rich poly(N-isopropylacrylamide (NIPAM)) shell layer was investigated as a function of pH, ionic strength and temperature. Adsorption of BSA protein onto such cationic and thermosensitive particles was found negligible below LCST of poly[NIPAM], whereas it was much higher above. In addition, the pH and the salinity dependence of the adsorbed amount at the plateau reflected the role of electrostatic interactions. Protein adsorption behavior was discussed by taking into account the changes in the interfacial properties of polymer particles (structure of the shell, hydrophilic-hydrophobic balance, charge density) versus temperature, suggesting that coulombic forces are mostly operating in this process. A desorption study showed that the BSA release efficiency was dependent upon the incubation time of the preliminary adsorbed step and the effect of pH and ionic strength confirmed the contribution of electrostatic interactions.

Key words: Cationic hydrophilic particles - Adsorption - BSA - Electrostatic interactions

Biorelevant Latexes and Microgels for the Interaction with Nucleic acids

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Table of Contents

Abstract

This chapter is a review of recent work devoted to polymer colloids in nucleic acids domain and principally in biomedical diagnostic, in which latex particles are used as carrier. After a brief introduction concerning the applications of latex particles in the biomedical field, the first part describes the routes leading to the elaboration of reactive latexes using radical-initiated polymerization in heterogeneous media. Secondly, the adsorption and the chemical grafting of nucleic acids are presented as a function of pH, ionic strength, surface charge density and cationic and anionic nature of particles surface. The good knowledge of the colloidal properties of latex latexes particles permits the well control of the immobilization process (adsorption and covalent binding) of functionalized single stranded DNA fragments (oligonucleotides). Finally, the last part briefly describes some fine applications based on latex-oligonucleotides in the specific capture of target DNA or RND and also on colloidal particles for separation and concentration nucleic acid molecules.

Colloidal vectors for delivery of bioactive molecules: surface modification by polymers

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Abstract: The elaboration of colloidal delivery agents, particles or emulsions, is the focus of many investigations. Numerous approaches are indeed currently developed in order to tune the physico-chemical properties of the carriers to better meet the needs of particular applications. In this context, a fairly recent stategy consists in using polymers bearing various functional groups to modify the interfacial properties of the carrier. This paper aims at reviewing the recent progresses achieved in this field with polymers of varied chemical nature, emphasizing on the characterization methods of the modified colloids and on the effects of the modes of binding and of the architecture of the polymers on the surface properties of the colloids.

Keywords: Colloidal carriers, polymers, adsorption, covalent grafting, surface derivatization, functional polymers, delivery agent.

Preparation and Characterization of (o/w) Magnetic Emulsions

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Abstract

This paper reports on the preparation of well defined (o/w) magnetic emulsions from an organic ferrofluid. The ferrofluid synthesis is first described and a complete characterization is achieved by using numerous techniques (elemental analysis, infrared spectroscopy, magnetic measurements, Mössbauer spectroscopy, X-ray diffraction, transmission electron microscopy). The ferrofluid is found to be composed of superparamagnetic maghemite nanoparticles, with a diameter below 10 nm, stabilized in octane by a surrounding oleic acid layer. This magnetic fluid is then emulsified in aqueous media in order to obtain stable ferrofluid droplets. The use of a couette mixer and a size sorting step under magnetic field allowed producing narrow sized magnetic emulsion. Morphology, chemical composition and colloidal properties of the emulsion are investigated. Magnetic properties of both ferrofluid and magnetic emulsion are also compared and discussed. In particular, it is showed that the superparamagnetic behavior is still observed after the emulsification process.

Keywords: Maghemite, ferrofluid, superparamagnetism, surfactant, magnetic emulsion.

Recent published papers:

Contribution to the International Polymer Colloids Group Newsletter

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Our activity on block copolymers, their colloidal properties and their application as polymeric surfactants was continued in 2002.

A review article on « Block Copolymer Micelles and Assemblies » by G. Riess, Ph. Dumas and G. Hurtrez was recently published in MML Series vol 5, 69-110 in CITUS books 2002 Editors R. ARSHADY – A. GUYOT. It contains chapters on controlled synthesis of block copolymers, their use in emulsion, microemulsion and dispersion polymerization, the biomedical and non-biomedical applications of block copolymer micellar systems.

Another review article « Micellization of block copolymers » was submitted recently to Progress in Polymer Science.

Publications :

1) « Synthesis of PMMA-g-PDMS graft copolymers via a miniemulsion process »
   J. F. Stumbé, F. Calderara, G. Riess
   Polymer Bulletin 47, 277-282 (2001)

2) « Mechanochemical synthesis of poly(butadiene–b-acrylic acid) »
   M. Popa, M. Daranga, G. Riess
   Europ. Polym. J. 38, 407-412 (2002)

Annual Report IPCG

F. J. Schork
August 2002

Recently Published Papers

Luo, Yingwu, F. Joseph Schork, Yulin Deng and Zegui Yan, " Emulsion/Miniemulsion Polymerization of Butyl Acrylate with the Cumene Hydroperoxide/Tetraethlenepentamine Redox Initiator" *Polymer Reaction Eng*. 9(3), 91-106 (2001).

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Luo, Yingwu and F. Joseph Schork, "Emulsion Copolymerization of Butyl Acrylate With Cationic Monomer Using An Interfacial Redox Initiator System," *J. Polymer Science Part A: Polymer Chemistry*, 39(16), 2696-2709 (2001).

Wu, X. Q, and F. J. Schork, "Kinetics of Miniemulsion Polymerization of Vinyl Acetate with Nonionic and Anionic Surfactants," *J. Appl. Polym. Sci*. 81, 1691-1699 (2001).

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Luo, Yingwu, and F. Joseph Schork, “Emulsion And Miniemulsion Polymerization with Oil-soluble Initiator In the Presence/Absence of an Aqueous-Phase Radical Scavenger*”, J. Polymer Science Part A: Polymer Chemistry*, 40(19), 3200-3211, 2002.

In Press

Tsavalas, John G. Yingwu Luo and F. Joseph Schork, "Grafting Mechanisms in Hybrid Miniemulsion Polymerization", *J. Appl. Pol. Sci.* (in press).

ABSTRACT: The ultimate objective of hybrid miniemulsion polymerization is to produce a water-based crosslinkable coating through *in-situ* grafting of a free-radical growing acrylic polymer with an unsaturated resin. Certain authors have reported low grafting while others have reported higher. This paper explores the factors that influence the grafting tendencies of these systems. Methacrylates such as methyl methacrylate (MMA) have a sterically hindered radical center that lowers its reactivity towards unsaturated resin. This steric hindrance from the methyl group forces grafting of this type of monomer to occur by abstraction of a hydrogen allylic to a resinous double bond. This chain transfer produces a relatively inactive radical on the resin that reduces the grafting efficiency. The transfer process also inherently produces some degree of terminated PMMA polymer within the particle. Grafting occurs in this type of system through termination of living PMMA chains with that radical produced on

the resin. For relatively water-soluble monomers such as MMA, grafting efficiency is further lessened by homogeneous nucleation resulting from the monomer hydrophilicity. These newly created particles cannot contain alkyd due to its hydrophobicity and thus inability to transport across the aqueous phase, and hence cannot produce grafted polymer. Nonetheless, degree of grafting of nearly 50% was observed in these systems. For hybrid systems involving an acrylate monomer such as butyl acrylate (BA), virtually complete grafting with alkyd was observed. This is due to the uninhibited BA radical center allowing the molecule to directly add through a resin double bond. This process offers the possibility for complete grafting. Homogeneous nucleation is also not involved in this system due to insolubility of BA in the aqueous phase. Resin double bond content, and degree of conjugation, also play an integral role in the grafting process.

Wu, X. Q., X. M. Hong and F. J. Schork, "Miniemulsion and Macroemulsion Copolymerization of Vinyl Acetate with Veova", *JAPS* (in press).

ABSTRACT: The miniemulsion and macroemulsion polymerization of vinyl acetate with vinyl versatate in batch and semibatch systems was investigated. Vinyl versatate was added either as an emulsion with the vinyl acetate, or as a neat liquid stream. In the batch runs, there is a poor dispersion of vinyl versatate during the nucleation period for the runs in which the vinyl versatate was added neat at the beginning of the polymerization. This led to smaller particles, lower polymerization rate and different polymer composition evolution when compared with runs in which the vinyl versatate was emulsified with the vinyl acetate. In seeded semibatch runs, residual surfactant in the seed latex, along with the propensity for homogeneous nucleation in vinyl acetate emulsions resulted in continuing nucleation during the entire semibatch interval. The polymerization rate was primarily affected by monomer feedrate rather than the feeding mode. The effect of monomer feeding mode on copolymer composition was weak when the semibatch feedrate was low, indicating some level of vinyl versatate mass transfer resistance. In all runs, only one glass transition temperature was observed, indicating effective copolymerization.

In Review

Tsavalas, John, and F. Joseph Schork, “The Morphology of Alkyd/Acrylate Latexes Produced Via Hybrid Miniemulsion Polymerization: Grafting Mechanisms”, *Progress in Colloid & Polymer Science* (in review).

ABSTRACT: The ultimate objective of hybrid miniemulsion polymerization is to produce a water-based crosslinkable coating through in-situ grafting of a free-radical growing acrylic polymer with an unsaturated resin. Certain authors have reported low grafting while others have reported higher. This paper explores the factors that influence the grafting tendencies of these systems. Methacrylates such as methyl methacrylate (MMA) have a sterically hindered radical center that lowers its reactivity towards unsaturated resin. This steric hindrance from the methyl group forces grafting of this type of monomer to occur by abstraction of a hydrogen allylic to a resinous double bond. This chain transfer produces a relatively inactive radical on the resin that reduces the grafting efficiency. Grafting occurs in this type of system through termination of living PMMA chains with that radical produced on the resin. For hybrid systems involving an acrylate monomer such as butyl acrylate (BA), virtually complete grafting with alkyd was observed. This is due to the uninhibited BA radical center allowing the molecule to directly add through a resin double bond.

Zegui Yan, Zegui, Yingwu Luo, Yulin Deng, And Joseph Schork, "Water-Soluble/Dispersible Cationic Pressure-Sensitive Adhesives Part 2. Adhesives from Emulsion Polymerization", ***JAPS*****, (in review).**

Abstract: In our previous work we reported that cationic water-soluble pressure sensitive adhesives could be synthesized in ethanol or methanol. These cationic water-soluble adhesives would not cause stickies problem during paper recycling and can be easily removed from the papermaking system by adsorbing on wood fibers. In this study, we report the synthesis and application of water based cationic pressure sensitive adhesives using miniemulsion polymerization. A redox initiator system of cumene hydroperoxide/tetraethylenepentamine was selected for miniemulsion polymerization. The end use properties of the psas were evaluated, and the repulpability of the psas in paper recycling was studied. It was found that the cationic psa from miniemulsion polymerization itself was insoluble or non-dispersible in water during the paper recycling process. However, if this water-insoluble cationic psa from miniemulsion was formulated with a water-soluble cationic psa made from ethanol, the solubility or dispersibility of the former psa in water was improved. The molecular weight and crosslinking degree of the psa polymer have significant effects on the psa properties and dispersability.

Tsavalas, John G. Yingwu Luo, Laila Hudda, and F. Joseph Schork, "Limiting Conversion Phenomenon in Hybrid Miniemulsion Polymerization", ***Polymer Reaction Engineering*****, (in review).**

ABSTRACT: A phenomenon seemingly unique to hybrid miniemulsion polymerization was observed where monomer conversion would either plateau at a limiting value or quickly switch to a dramatically lesser rate. A limiting conversion in the field of polymerization, per se, is not in itself unique; rather the principles leading to this particular observed form. This phenomenon has been attributed to a combination of three factors. The first factor is the degree to which the monomer and resinous component are compatible. Second is the resultant particle morphology after circa 80% monomer conversion, which roughly corresponds to the portion of reaction where this morphology is established. The degree of interaction between the growing polymer and resin (grafting) comprises the third factor. Of these three, the first two factors were found much more significant in contributing to the limiting conversion. When particle morphology was found to be core/shell, a hard shell (high T_g polymer, PMMA) was found to form a barrier against newly formed initiator radicals derived in the aqueous-phase after appropriate conversion. Residual unreacted monomer solubilized in the resin-dominated particle core was thereafter unreachable by new radicals; hence a limited monomer conversion. In cases where the acrylic polymer (PBA) exhibited a glass transition significantly below the reaction temperature, instead of a core/shell morphology one where the acrylic polymer (and monomer) comprised the continuous particle-phase with small internal resinous island domains was observed. A portion of the monomer concentration was again found to be solubilized within the resin domains, yet in this case newly

formed initiator radicals encountered a viscous environment instead of an effective barrier. Rate was found to be limited by the feed of monomer to local polymerization in the continuous particle phase from those resinous islands where residual monomer is solubilized. This is what led to continued polymerization, but at a considerably lesser rate.

Theses

John Tsavalas, "Molecular Level Investigations in Hybrid Miniemulsion Polymerization," PhD, December, 2001.

ABSTRACT

In the field of hybrid miniemulsion polymerization, work prior to this thesis was dominated by proof-of-concept studies. The incentive and objective of the current research was to address lingering issues from those prior studies and to develop a more fundamental understanding of the hybrid grafting mechanism and the connections between reaction phenomena and product characteristics.

A strong dependence was found between monomer structure and the degree of grafting possible in hybrid miniemulsion polymerization. Monomers that had a sterically hindered radical center were found to prefer resin attack through chain transfer where monomers with an uninhibited radical center were found to favor direct addition to resin double bonds. Based solely on those routes of attack, virtually complete grafting was achieved with direct addition to double bonds where a lower degree of grafting was observed when attack was facilitated through chain transfer. The lower degree of grafting in those systems was also exacerbated by homogeneous nucleation (from hydrophilic monomer) inherently creating particles absent of alkyd (due to its hydrophobicity and inability to transport to those new particles).

Particle morphology was found most influenced by compatibility of the comprising components. A type of core/shell morphology was observed, when there was incompatibility between the acrylic polymer and resin, where the shell was a glassy acrylic phase. With better component compatibility, aided in part by more efficient grafting, a particle morphology developed consisting of a continuous acrylic/polyacrylic particle phase with internal island domains of resin. Those particle morphologies were found directly correlated to different limiting conversion phenomena observed for the acrylic monomer. In systems where radicals were derived in the aqueous phase and a glassy shell developed after intermediate conversion, newly formed radicals encountered a barrier to entry and monomer solubilized in the resin core of the particle was thus residual; hence a limiting conversion. Instead, when the island domain morphology developed, monomer conversion was found limited by the rate of transport out of the island domains to the local sites of polymerization in the continuous particle phase along with the viscosity of that phase.

The proposed use of living polymerization was to create model compounds of the hybrid grafted polymer with which to compare to those created under normal conditions. Living polymerization via a miniemulsion had yet to be documented and it was quickly found that the original intention of that portion of study would not be able to be pursued. Miniemulsions were found unstable when the living agent was present during polymerization. In light of this, pioneering research was performed which led to

fruitful observations and a better understanding of that field. It was first found by experiment that substitution of a nonionic surfactant for ionic led to stable miniemulsions and polymers of controlled architecture. Next, it was observed that the domination of early molecular weight distribution by oligomeric species was largely contributing to miniemulsion instability. Finally, through a theoretical analysis, it was confirmed that the presence of oligomers could lead to conditions where monomer droplets might achieve a super-swelling state, after which coalescence and hence instability was inevitable. The theoretical analysis also accounted for the beneficial effect of substituting the nonionic surfactant through a lowering of the monomer chemical potential in the droplets. Under those conditions, a super-swelling state was unfavorable and miniemulsion stability could be retained.

Contribution to IPCG Newsletter

Stan Slomkowski, Center of Molecular and Macromolecular Studies, Lodz, Poland

Recently published papers

1. S.Sosnowski, M.Gadzinowski, S.Slomkowski
   Biodegradable, monodisperse nano- and microspheres forming stable suspension in water media
   Annals of the Polish Chemical Society Year 2001, 281-281 (2001)

2. Stanislaw Slomkowski, Beata Miksa, Teresa Basinska, Anamika G.Gambhir, Arun Kumar, Bansi D. Malhotra
   Polymer microspheres with immobilized enzymes and other proteins as materials for biosensors
   Biocybernetics and Biomedical Engineering, 21, 49-65 (2001)

3. S.Sosnowski, S.Slomkowski, A.Lorenc, H.R.Kricheldorf
   Mechanism of dispersion polymerization of L-lactide initiated with 2,2-dibutyl-2-stanna-1,3-dioxepane
   Colloid Polym Sci, 280, 107-115 (2002)

4. A.Azioune, M.M.Chehimi, B.Miksa, T.Basinska, S.Slomkowski
   The hydrophobic protein-polypyrrole interactions: the role of van der Waals and Lewis acid-base forces as determined by contact angle measurements
   Langmuir, 18, 1150-1156 (2002)

5. Stanislaw Slomkowski, Stanislaw Sosnowski, Mariusz Gadzinowski
   Dispersion Polymerization of Lactides and.-Caprolactone
   Polimery, 7.8, 485-490 (2002)

6. S.Slomkowski, B.Miksa, D.Kowalczyk, T.Basinska, M.M.Chehimi, M.Delamar
   Polymeric microspheres and related materials for medical diagnostics
   Medical Diagnostic Science and Technology, W.-T. Law, N.Akmal, A.M.Usmani (eds), Marcel Dekker, New York, 2002, 393-412.

Papers in press

New Types of Microspheres and Microsphere Related Materials for Medical Diagnostics

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Polym. Adv. Technologies, in press

Abstract

Polymer microspheres are used in diagnostics as “reagents” and as elements of diagnostic devices. In this paper we compare properties of microspheres with aldehyde, carboxyl and hydroxyl groups in their surface layers. Microspheres with aldehyde groups were obtained by radical emulsion copolymerization of styrene and acrolein and in sequential redox polymerization of pyrrole followed with radical polymerization of acrolein. Microspheres with hydroxyl groups were synthesized by radical emulsion copolymerization of styrene and α-*t*-butoxy-ω-vinylbenzyl-polyglycidol macromonomer. Microspheres with hydroxyl and carboxyl groups were synthesized by radical emulsion copolymerization of methylmethacrylate, acrylic acid and 2-hydroxyethylmethacrylate. X-Ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) revealed that microspheres had the core-shell morphology with surface layers enriched in polymeric units with reactive groups. The mentioned above microspheres were used as supports for adsorption and covalent immobilization of human and animal proteins - human serum albumin (HSA), gamma globulins (γG; human, rabbit and goat), human fibrinogen (Fb), and enzymes – glucose oxidase (GOD) and urease (Urs). Applicability of microspheres with attached antigens and/or antibodies (γG) for turbidimetric aggregation tests and for new type of test based on changes of electrophoretic mobility of microspheres is discussed. Potential applications of microspheres with immobilized enzymes for construction of biosensors are described.

Preparation of Biodegradable Particles by Polymerization Processes

Stanislaw Slomkowski

Submitted, Chapter in Colloid Polymers: Preparation and Biomedical Applications, ed. A.Elaissari, Marcel Dekker

Summary

Biodegradable polyester microspheres found many applications in fundamental studies in biology and in pharmacy as drug delivery carriers. Often it is essential to use particles with well determined diameters, diameter distribution, molecular weight and crystallinity of constituting polymers. This chapter describes fundamental features of the pseudoanionic and anionic polymerizations of ε-caprolactone and lactides leading to product in form of microspheres. Recipes allowing synthesis of microspheres are given, There are discussed models of microsphere nucleation and growth and experimental results indicating formation of microsphere nuclei at the very beginning of polymerization followed with propagation inside of microspheres. Formal kinetics of ionic and/or pseudoionic dispersion polymerizations of cyclic esters are analyzed. On the basis of these analyses differences between rates of polymerization in solution and in dispersed systems are explained. Methods suitable for control of degree of crystallinity of poly(L,L-lactide) microspheres in a broad range from 0 to 60 % are described. There is described also a method allowing transfer of microspheres from organic liquids (in which they are synthesized) into the water based media in which they form stable suspensions. Strategies of entrapment/attachment of bioactive compounds (including proteins) to poly(ε-caprolactone) and polylactide microspheres are discussed and the corresponding examples are given.

Covalent Immobilization of Urease to Polypyrrole Microspheres for Application to Urea Biosensor

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Submitted to e-Polymers

Abstract

Urease has been covalently immobilized onto polypyrrole(PPY) microspheres chemically linked to conducting polypyrrole-polyvinyl sulphonate (PPY-PVS) films. Conducting polypyrrole-polyvinyl sulphonate films were electrochemically prepared for 5-7 minutes at a constant current of 2mA using indium-tin-oxide (ITO) glass plates(surface area 1x1cm^2) as working electrode and standard calomel electrode as the reference electrode. Urease covalently linked to polypyrrole microspheres (by reaction of protein amino groups with microsphere surface aldehyde groups of the surface of microspheres) was entrapped/adsorbed onto electrochemically prepared conducting polypyrrole polyvinyl sulphonate films deposited on ITO. Potentiometric measurements undertaken on these conducting polymer electrodes using an ammonium ion analyzer reveal that these can be used for estimating urea concentration in solutions from 5 mM to 60 mM.

International Polymer Colloids Group Newsletter

Eric S. Daniels, Victoria L. Dimonie, Mohamed S. El-Aasser,
Andrew Klein, Cesar A. Silebi, and E. David Sudol

Emulsion Polymers Institute
Lehigh University, Iacocca Hall, 111 Research Drive
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Recent Publications

Dispersion Polymerization of *n*-Butyl Acrylate, D. Wang, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, *J. Appl. Polym. Sci,.* **84**, 2692 - 2709 (2002).

The dispersion polymerization of *n*-butyl acrylate (BA) was investigated using alcohol/water mixtures as the dispersion medium, 4,4'-azobis-(4-cyanopentanoic acid) as the initiator, and polyvinylpyrrolidone (PVP) as the stabilizer. The effects of polymerization parameters, such as alcohol/water ratio in the medium, and type and concentration of polymeric stabilizer, on the resulting particle size and size distribution were studied. The final particle size and the stability of the dispersion system were found to be greatly influenced by the type of alcohol used in the mixture, i.e., methanol or ethanol, even through the apparent solubility parameters are almost the same for the two types of mixtures. PBA particles with controlled size, size distribution (monodisperse), and gel content were successfully prepared in a 90/10 methanol/water medium. It was found that the relationship between the particle size and the initiator concentration in the dispersion polymerization of BA is the reverse of those for similar PSt and PMMA systems (i.e., the particle size decreased with increasing initiator concentration).

Seeded Dispersion Polymerization, D. Wang, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, *J. Appl. Polym. Sci.,* **84**, 2710 - 2720 (2002).

Micron-size poly(*n*-butyl acrylate) (PBA) and polystyrene (PSt) particles were used as seed in second-stage seeded dispersion polymerizations. The effects of various polymerization parameters on the morphology of the structured particles resulting from the second-stage seeded dispersion polymerizations were studied, and a series of uniform micron-size structured particles were successfully prepared. In addition to the polymerization medium, the type of stabilizer (i.e., the molecular weight of the PVP stabilizer) that was used in the seed preparation and the subsequent seeded dispersion polymerization was found to be important. The final outcome of a seeded dispersion polymerization, i.e., the morphology of the structured particles and the formation of secondary particles, was found to be primarily governed by thermodynamic factors. It was also found that the latex particles in these dispersion systems are virtually stabilized by the small amount of grafted PVP molecules; the dispersions maintain colloidal stability after repeated washing of the particles, which removes all of the soluble PVP.

Effect of PVP in Dispersion and Seeded Dispersion Polymerizations, D. Wang, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, *J. Appl. Polym. Sci.,* **84**, 2721 - 2732 (2002).

The outcome of seeded dispersion polymerizations of *n*-butyl acrylate (BA) and styrene (St) in terms of the success of growing the seed particles without nucleating new particles or generating coagulum was found to be dependent on the seed type (PBA or PSt), the second stage monomer (BA or St), and the type of polyvinylpyrrolidone (PVP) stabilizer (PVP K30 or PVP K90). All seeds were first cleaned of excess stabilizer by medium-replacement prior to the seeded polymerizations. In general, successful particle growth was achieved when the second stage polymerization employed PVP K30 (1 wt%) as the stabilizer. In contrast, nearly all reactions employing PVP K90 (1 wt%) as the second stage stabilizer resulted in the nucleation of a second crop of particles. These phenomena were further investigated by carrying out dispersion polymerizations using the supernatant obtained by separating the seeds from the second stage media (containing monomer). The results paralleled those in the seeding studies and were explained by the presence of small amounts of grafted PVP created in situ during the preparation of the seeds.

Influence of Particle Surface Properties on Film Formation from Calcium Precipitated Carbonate/Latex Blends, J. Tang, M. Kamson, E. S. Daniels, V. L. Dimonie, A. Klein and M. S. El-Aasser, *J. Appl. Polym. Sci.*, **86**, 891 - 900 (2002).

The surface properties of films prepared from a blend of precipitated calcium carbonate pigment (PCC) and poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) [P(BMA/BA); T_g = 0 °C] latex were investigated in terms of the surface characteristics of the PCC and P(BMA/BA) latex particles. It was found that the presence of carboxyl groups on the P(BMA/BA) latex particles significantly improved the uniformity of the distribution of the PCC particles within the P(BMA/BA) copolymer matrix and the gloss of the resulting films. This phenomenon could be explained by an acid-base reaction between the PCC particles and the carboxylated P(BMA/BA) latex particles. Studies on the influence of the composition of PCC/P(BMA/BA) latex blends on the gloss and transparency of the films were also performed, which led to the determination of the critical pigment volume concentration (CPVC) of this system which was found to be 42 vol%.

Study of the Preparation and Mechanism of Formation of Hollow Monodisperse Polystyrene Microspheres by SPG (Shirasu Porous Glass) Emulsification Technique, G. H. Ma, S. Omi, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, *J. Appl. Polym. Sci,* **85**, 1530 - 1543 (2002).

In a previous study, it was found that monodisperse polystyrene (PSt) hollow particles can be prepared under special conditions by combining a Shirasu Porous Glass (SPG) emulsification technique and subsequent suspension polymerization process. That is, a mixture of styrene (St), *N*,*N*-dimethylamino ethyl methacrylate (DMAEMA), hexadecane (HD), and initiator *N*,*N'*-azobis(2,4-dimethylvaleronitrile) (ADVN) was used as the dispersed phase in an aqueous phase containing poly(vinyl pyrrolidone) (PVP), sodium lauryl sulfate (SLS), and water-soluble inhibitor. The dispersed phase was created by pushing the oil phase through the uniform pores of an SPG membrane into the continuous phase to form uniform droplets. Then, the droplets were polymerized at 70°C. It has been puzzling that hollow microspheres were obtained only when sodium nitrite ($NaNO_2$) was used as a water-soluble inhibitor, while one-hole particles were formed when hydroquinone (HQ) or diaminophenylene (DAP) were used. In this study, the mechanism of formation of the hollow microspheres was verified by measuring the variation of diameter, molecular weight distribution, and monomer conversion, and by observing morphological changes during the polymerization, as well as by changing the type and amount of hydrophilic monomer, and initiator. It was found that the diameter of the oil droplets decreased and a large amount of secondary new particles formed immediately after polymerization started in the case of $NaNO_2$. However, there was no such apparent behavior to be observed when HQ or DAP was used. It was determined that the hollow particles formed due to the rapid phase separation between PSt and HD, and as a consequence, a large amount of monomer diffused into the aqueous phase to form the secondary particles. Rapid phase separation confined the HD inside the droplets, a non-equilibrium morphology. On the other hand, one-hole particles, representing an equilibrium morphology, formed when the phase separation occurred slowly because a lot of monomer existed inside of the droplets to allow mobility of the PSt. The addition of DMAEMA allowed the hollow particles to be formed more easily by decreasing the interfacial tension between the copolymer and aqueous phase.

Surfactant Concentration Effects on Nitroxide-Mediated Living Free Radical Miniemulsion Polymerization of Styrene, G. Pan, E. D. Sudol, V. L. Dimonie, and M. S. El-Aasser, *Macromolecules*, **35**, 6915 - 6919 (2002).

TEMPO-terminated oligomers of polystyrene (TTOPS) are being used as a macro-initiator to initiate the miniemulsion polymerization of styrene at 125 °C. In this work, the surfactant concentration (Dowfax 8390) used to prepare the miniemulsion was varied from 1.25 to 25 mM. It was found that with increasing surfactant concentration, the particle size decreased and the particle number increased as expected. However, this variation in the surfactant concentration and its effect on the number of particles generated had little effect on the resulting polymerization rate and polymer molecular weight in the nitroxide-mediated miniemulsion system. The average numbers of active and stable free radicals per particle were estimated and used to explain the kinetic differences between living free radical miniemulsion polymerization and normal free radical emulsion polymerization.

Review of Polystyrene Diffusion Studies in Latex Particles by Small-Angle Neutron Scattering, S. D. Kim, A. Klein and L. H. Sperling, *Polym. Adv. Technol.,* **13**, 403 - 412 (2002).

This paper reviews small-angle neutron scattering (SANS) and some results from direct nonradiative energy transfer (DET), for the observation of the diffusion coefficients of polystyrene chains at latex interfaces. To compare SANS with DET, doubly labeled polystyrene with deuterium and fluorescence groups were synthesized, showing that while SANS and DET produce comparable data in terms of diffusion coefficients, both results differ in detail, each having their own advantages. Chain confinement, ionic end groups, and short branch effects on interdiffusion were studied. Large polymer chains confined in small particles have non-Gaussian shapes that store rubber elastic energy. Rapid, non-diffusion relaxation is inhibited because the density would be required to become less than normal. Hence confinement effects on the diffusion rate are not significant. Using the DET method, ionic end-groups were found to increase the early-time apparent interdiffusion coefficients during film formation. The early-time apparent diffusion coefficients of polystyrene with varying end-groups were found to increase as follows:

$$H < COOH < SO_4$$

The higher apparent diffusion coefficients of the chains with ionic groups are presumably due to a surface segregation of the

end-groups caused by the polar, aqueous environment during latex synthesis. The interdiffusion behavior of sulfite-ended polystyrene ($M_n \cong 300\,000$ g/mol) with H-ends, one sulfite end, and two sulfite ends were compared *via* SANS and DET. The diffusion coefficients of polystyrene with one or two sulfite end groups were five times and ten times lower than that of polystyrene, respectively. The ionic end group effects on the *reduced* diffusion coefficients are interpreted as the competition between enhancement by the surface segregation of end groups and reduction by end group aggregation. Noting that *sulfate* end groups diffused faster, while *sulfite* end groups diffused slower, the effect is complex, and not yet fully resolved. Diffusion coefficients of polystyrene with branches were studied by DET. Short branches work to decrease the T_g and hence

increase the diffusion coefficients. However, after the experimental temperature, T, is converted to a normalized temperature, $T - T_g$, the diffusion coefficients are found to be almost independent upon the number of branches and the length of branches. The branch length ranged from one-carbon to 40 carbons. Side chains of entanglement molecular weight or longer may be required to significantly reduce the diffusion coefficient.

Publications Accepted

Towards an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of Styrene-Butadiene-Acrylic Acid. Separation and Characterization of the Water-Soluble Oligomers, X. Y. Yuan, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, accepted by *Macromolecules*

A series of techniques was developed to quantitatively characterize the free water-soluble oligomers found in the aqueous phase in a model styrene/butadiene/acrylic acid (St/Bu/AA) batch emulsion terpolymerization process. Particular attention was paid to the early stages of the polymerization. Ultracentrifugation was used to accomplish the separation of the aqueous phase from the particle phase. ^{1}H NMR, aqueous phase GPC, and GC techniques were used to determine the oligomer concentration as well as their composition and the surfactant concentration in the aqueous phase, the oligomer molecular weight, and the acrylic acid monomer conversion, respectively. The results were related to the overall conversion and the number of particles as a function of conversion. The oligomer concentration vs. conversion curves for the model system show a maximum at around 12% conversion. However, the position of this maximum with respect to conversion is related to the surfactant concentration. The sharp decrease in the oligomer concentration after micelles disappeared and the decrease in the number of particles was considered to have resulted from a strong interaction of these oligomers, which are rich in St and Bu units, with the polymer of the latex particle surface. Increasing the AA concentration in the recipe increased the water-soluble oligomer concentration and the number of particles, thereby increasing the rate of polymerization.

Towards an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of Styrene-Butadiene-Acrylic Acid. Function of Carboxylic Acid, X. Y. Yuan, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, accepted by *J. Appl. Polym. Sci*

In a further effort to understand the role of water-soluble oligomers formed during the emulsion terpolymerization of styrene/butadiene/acrylic acid, the reaction temperature, initiator concentration, and ionic strength were varied and the kinetics and resulting oligomers were characterized as a function of reaction time. The rate of polymerization (R_p) was observed to increase with increasing temperature and initiator concentration; the reasons for this vary. The increase in R_p with increasing initiator concentration is mainly due to the increase in the number of oligomeric radicals formed, and subsequently, the resulting number of particles (N_p). Increasing the temperature increases the water-solubility of both monomers and polymers, which results in changes in the composition and molecular weight of the oligomeric radicals being formed. The primary reaction locus in the St/Bu/AA system was noted to shift to the aqueous phase after most of the styrene and butadiene had reacted, based on the unreacted AA profile. The role of water-soluble oligomers (both oligomeric radicals and dead oligomers) during the emulsion polymerization of St/Bu with acrylic acid can be described by three periods: (1) particle generation, and (2) before and (3) after the critical surface saturation concentration (CSSC) is reached during the particle growth period. The incorporation of AA monomer into the oligomer chains after the CSSC may cause destabilization of the latexes through a bridging flocculation mechanism.

Towards an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of Styrene-Butadiene-Acrylic Acid. Mechanisms of Water-Soluble Oligomer Formation, X. Y. Yuan, V. L. Dimonie, E. D. Sudol, J. E. Roberts, and M. S. El-Aasser, accepted by *Macromolecules*

The mechanism of water-soluble oligomer formation during the emulsion terpolymerization of styrene/butadiene/acrylic acid differs depending on whether the surfactant concentration is above or below the cmc. A growth mechanism for the water-soluble oligomers involving reactions in both the aqueous and organic phases for polymerizations carried out above the cmc of SLS is proposed. This is used to explain why the fraction of butadiene (Bu) units in the water-soluble oligomer chains is the highest compared to the styrene or even the acrylic acid (AA), despite the low water solubility of Bu monomer relative to AA. The supporting evidence for this mechanism includes: (1) the increase in the oligomer molecular weight with increasing initiator concentration, as in the case of polymerization occurring in micelles, indicating that the oligomers had grown in an isolated organic phase; and (2) the much higher fraction of AA homo dyads found in the oligomers formed at an SLS concentration below the cmc compared to that above the cmc. These results indicate that, in the absence of micelles, the oligomers will grow in the aqueous phase and result in more AA block dyad sequence units in the oligomer chains owing to the higher AA monomer concentration there. When micelles exist, the water-soluble oligomers will grow in both the aqueous phase *and* the organic phase. In this case, fewer AA dyads will be noted.

Synthesis of Well-Defined, Functionalized Polymer Latex Particles Through Semi-Continuous Emulsion Polymerization Processes, J. Tang, T. Ding, E. S. Daniels, V. L. Dimonie, A. Klein, and M. S. El-Aasser, accepted by *J. Appl. Polym . Sci.*

A design of a semi-continuous emulsion polymerization process, primarily based on theoretical calculations, was carried out with an objective of achieving overall independent control of latex particle size, monodispersity in particle size distribution, homogeneous copolymer composition, the concentration of functional groups (e.g., carboxyl groups), and glass transition temperature using *n*-butyl methacrylate (BMA)/*n*-butyl acrylate (BA)/methacrylic acid (MAA) as a model system. The surfactant coverage on the latex particles is very important in maintaining a constant particle number throughout the feed process, which results in the formation of monodisperse latex particles. A model was set up to calculate the surfactant coverage from the monomer feed rate, surfactant feed rate, desired solids content, and particle size. This model also led to an equation that correlates the polymerization rate to the instantaneous conversion of the monomer or comonomer mixture. The use of this equation can determine the maximum polymerization rate, below or equal to which monomer-starved conditions can only be achieved. The maximum polymerization rate provides guidance for selecting the monomer feed rate in the semi-continuous emulsion polymerization process. The glass transition temperature of the resulting carboxylated poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) [P(BMA/BA)] copolymer can be adjusted by the varying the composition of the copolymers using the linear Pochan equation.

Properties of *n*-Butyl Methacrylate Copolymer Latex Films Derived from Crosslinked Latex Particles, H. M.. Ghazaly, E. S. Daniels, V. L. Dimonie, A. Klein, L. H. Sperling, M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*

Films obtained from copolymer latexes of *n*-butyl methacrylate (BMA) with a series of crosslinking monomers, i.e., a macromonomer crosslinker (Mac), ethylene glycol dimethacrylate (EGDMA), or aliphatic urethane acrylate (AUA) exhibited differences in their tensile properties and swelling behavior. In the case of P(BMA-co-EGDMA) copolymer, a dependence on initiator type was obtained. It is postulated that the network microstructures for the various copolymers evolved as the result of the copolymerization reactions between the monomer pairs during the synthesis in the miniemulsion free-radical copolymerization. These network microstructures are therefore hypothesized to influence the mechanical properties of the resultant films. Copolymers prepared with Mac were tough in comparison with copolymers made with EGDMA. The presence of longer linear or lightly-crosslinked PBMA chains and the looseness of the crosslinked network structures in the (PBMA-co-Mac) copolymers appear to be the factors responsible for the differences. All of the copolymer films disintegrated into swollen individual microgels when they were immersed in THF.

Direct Miniemulsification of Kraton Rubber/Styrene Solution: I. Effect of Manton-Gaulin Homogenizer, Sonifier, and Membrane Filtration, P. Jeong, V. L. Dimonie, E. S. Daniels, M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*

A direct miniemulsification process was utilized to prepare an artificial latex from Kraton® D1102 thermoplastic elastomer. The Kraton rubber was dissolved in styrene monomer, emulsified in an aqueous surfactant solution in the presence of a costabilizer using a sonifier, Manton-Gaulin homogenizer, and membrane filtration. Each miniemulsion droplet contained 20 wt% Kraton rubber in styrene, and thus, the Kraton rubber particle size and size distribution can be used to estimate the droplet size and size distribution of the miniemulsion. It was found that Kraton rubber particles obtained using the Manton-Gaulin homogenizer had an extremely broad size distribution ranging from 20 nm to 2 μm. The use of cetyl alcohol costabilizer produced Kraton rubber particles with a narrower size distribution by lowering the interfacial tension between the oil and aqueous phases, compared to the use of hexadecane as costabilizer. The broad size distribution of the Kraton rubber particles could be narrowed by employing a membrane filtration technique. However, small miniemulsion droplets remained undisturbed in the miniemulsion since they easily passed through the pores of the filter. These small droplets resulted from the sonification process conducted prior to the use of the membrane filtration process. The Kraton rubber particle size distribution became narrow with an increase in the sonifier duty cycle due to the viscoelastic behavior of the oil phase.

Recent Ph.D. Dissertations

Nanosize Latex Particles via Miniemulsion Polymerization

Christopher D. Anderson

The mechanisms of miniemulsion formation, stabilization, and polymerization were studied both experimentally and theoretically. The subdivision of miniemulsion droplets was investigated as a function of homogenization energy. The stabilization of droplets against Ostwald ripening has been explained on a thermodynamic basis. Miniemulsions and their corresponding latexes were synthesized and characterized for particle size and surface coverage by surfactant titration, as well as polymerization rate using calorimetry. Equations relating the surface properties and reaction kinetics to particle diameters were developed. The particle nucleation mechanism was established under varying free surfactant conditions. Nanosize latex particles (< 50 nm) have been synthesized using less surfactant and/or costabilizer than previous researchers.

The interfacial area in a miniemulsion prepared by sonification increased linearly with time according to an energy balance equation, and the droplets were shear-limited in size. Droplet diameters were reduced substantially after a single pass through a Microfluidizer, but did not change significantly after additional passes, indicating that the droplets were surfactant-limited in size.

Miniemulsion droplets were stabilized more effectively against Ostwald ripening by increasing the costabilizer amount or decreasing the costabilizer molecular weight. The initially broad droplet size distribution narrows considerably during polymerization as the result of monomer redistribution by a polymer concentration gradient. Hexadecane was more effective as a costabilizer than cetyl alcohol or predissolved polymer, and stabilized the miniemulsion droplets over a period of several hours.

The free surfactant concentration increased as surfactant was added, until the critical micelle concentration was exceeded at 60 mM SLS, and micellar nucleation occurred simultaneously with droplet nucleation. Most of the surfactant was on the surface of the droplets (80%) or particles (95%). The fractional surface coverage on the droplets was the same as on the corresponding latex particles. The droplet diameter in a low-solids miniemulsion was greatly reduced as a result of the high ratio of surfactant to monomer. The maximum rate of polymerization varied with the number of particles to the 0.59 power, and the kinetics were explained mathematically as an extension of Smith-Ewart kinetics. The rate of miniemulsion polymerization was expressed as a function of temperature using an Arrhenius equation.

Living Free Radical Miniemulsion Polymerization of Styrene

Gaofeng Pan

TEMPO-controlled living free radical polymerization was studied in miniemulsion system in this research. TTOPS were synthesized, and used in miniemulsion polymerization of styrene as macro-initiator. It was found that the polymerization rate is low (80% to 90% conversion after 24 hours polymerization). Molecular weight increases linearly with increasing conversion, and is narrow distributed (PDI (M_w/M_n) = 1.2~1.4 in well-controlled system). The measured molecular weights were close to the theoretically expected values up to 50% conversion, and deviation observed when conversion exceeded this level. The effect of TTOPS concentration was studied and found that the polymerization rate is independent to the TTOPS concentration. Lower molecular weights, with narrower distribution, were obtained with higher initial TTOPS concentration.

Particle size and size distribution were measure by CHDF and TEM. Broad particle size distribution was found. Particle size distribution was directly affected by the miniemulsion preparation method. Particle number was found to increase with conversion at high surfactant concentration ([DowFax-8390] > 10 mM), and constant at low surfactant concentration ([DowFax-8390] < 5 mM). With increasing surfactant concentration, the particle size decreased and the particle number increased. However, different surfactant concentrations had little effect on the molecular weight and the polymerization rate. Average number of active radical per particle ($\bar{n}$) in the concerned system was calculated by different methods. $\bar{n}$ was estimated to be in the level of 0.003.

The thermal self-initiation of styrene monomer was studied with the presence of TEMPO radicals at the polymerization temperature (125 °C). Induction period was observed in styrene auto-polymerization with TEMPO radicals and the length of the induction period was found to increase linearly with increasing initial TEMPO concentration. The thermal initiation rate during the induction period was found to be 10 times higher than that reported in bulk (no TEMPO). Identical relationships between the length of the induction period and the initial TEMPO concentration were found for the miniemulsion and corresponding bulk systems. Faster initial polymerization rates were found in bulk than in the corresponding miniemulsion system. This difference can be explained by different thermal initiation rates resulting from different thermal initiation efficiencies.

Poly(styrene-block-*n*-butyl acrylate) copolymers were prepared living free radical miniemulsion polymerization in the presence of ascorbic acid. It was found that the polymerization rate increased with increasing ascorbic acid concentration. A certain fraction of the polystyrene chains was dead at the beginning of the second step of polymerizations and did not participate in chain extension with *n*-butyl acrylate. The percentage of dormant TTOPS-1500 chains decreased with increasing ascorbic acid concentration.

International Polymer Colloids Group
2002 Newsletter Contribution
University of New Hampshire

Round Robin Study for Latex Particle Morphology Determination

Jeffrey Stubbs and Donald C. Sundberg

Over the course of our research work on latex particle morphology it has become increasingly clear that there is often a great deal of difficulty in determining the particle structure with certainty. A “round robin” study has been performed in which three different composite latex samples possessing unknown particle morphologies were produced and then distributed to various laboratories for independent morphology determination using various techniques. Other participants in the study in addition to our own laboratory were from Lund University, Atofina, Mitsubishi Chemicals, NeoResins and UCB Chemicals. The analysis techniques used were TEM (both whole particle and microtomed sections), SEM, cryo-fracture SEM, AFM, surfactant titration, DSC and solid state NMR. Whenever possible each method was performed by at least two different labs. The results test several questions including 1) the ability to reach firm conclusions about the particle morphology of systems of varying complexity, 2) the agreement between different labs for the same technique and 3) the agreement between conclusions about morphology from different techniques.

The results showed that for systems that are relatively simple to analyze it is possible to reach firm conclusions about the particle morphology, but that even in these cases several different techniques are required. For more difficult systems, even when using a multitude of techniques some questions may remain unanswered regarding certain details of the particle structure. The usefulness of a given technique is very dependant on the system under investigation. For instance, TEM is not very useful when the polymers cannot be selectively stained for phase contrast, while surfactant titration is not very useful when the seed and second stage polymers are of very similar polarity.

The agreement between different labs for the same analysis technique was generally very good. The most variation between results from different labs was experience for TEM. This seems to result from the importance of the sample preparation techniques used prior to the observation in the TEM, which may alter the way the samples appear when viewed in the microscope. This has brought up questions about the effect of embedding before microtoming and the staining techniques, and has spawned a separate study in which we are investigating various sample preparation methods used in TEM and how this relates to the determination of latex particle morphology.

Agreement between the results of different techniques was also found to be good, but perhaps a better way to explain this is that different techniques are complimentary rather than in agreement. Often a certain feature about the particle morphology can only be suggested by one method, and another complimentary technique is required to actually confirm this feature. For instance, when a large amount of interfacial material is detected by DSC or solid state NMR analysis this suggests the possibility of a highly occluded morphology which possesses a large amount of interface between the two polymers. However, a technique such as microtomed TEM, that visually reveals the internal structure of the particle, is required for confirmation of this feature and to provide more detailed information such as the location of the phase separated domains.

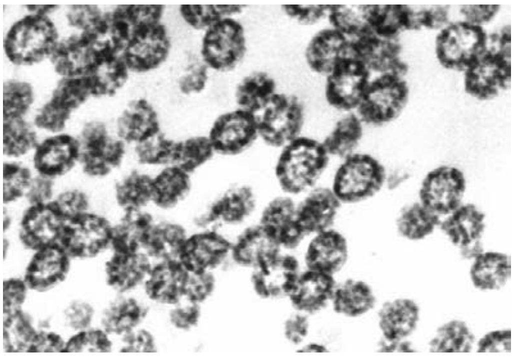
At least three different methods are usually required to answer three important questions about the particle structure. The first question is which polymer (or both and to what extent) is present on the outside surface of the particle. Surfactant titration is perhaps the most useful and simple technique to answer this question but is not useful under some conditions. Another possible technique may be XPS. The second question is regarding the shape of the particle (spherical, lobed, rough surface). Techniques such as AFM, SEM or whole particle TEM are useful in this case. Finally, the third question concerns the internal structure of the particle and in this case methods such as DSC, solid state NMR and microtomed TEM may provide complimentary answers.

This study has confirmed that the determination of particle latex morphology is by no means straightforward. Results can often be misleading and independent confirmation based on results from a complimentary technique is required to reach a firm conclusion. It is also crucial to consider the procedures that were followed to prepare samples for a given analysis and the possibility that these may have effected a change in the morphology.

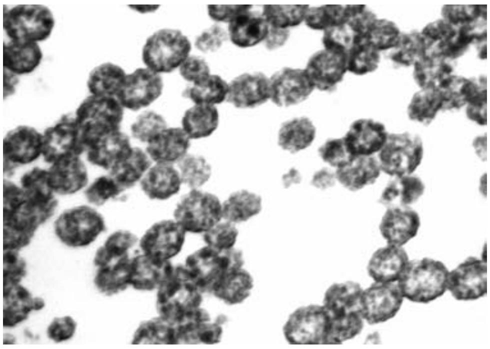
The Effect of Chain Transfer Agent on Particle Morphology Development under Kinetically Controlled Conditions

Jeffrey Stubbs and Donald C. Sundberg

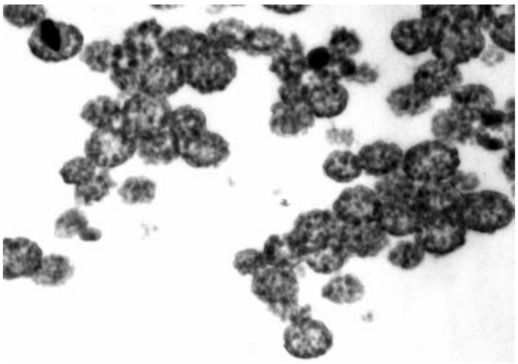
It is now understood that particle morphology development under kinetically controlled conditions is controlled in large part by the rate that radicals entering from the water phase can diffuse into the particles. Simple modeling has shown that the majority of the distance that the radicals diffuse occurs very soon after entry before the radical chain has grown significantly, since the center of mass diffusion coefficient decreases rapidly with increasing chain length. This suggests that the use of chain transfer agents (CTA) may have a large effect on particle morphologies. Short, mobile radicals created by transfer reactions diffuse more rapidly and may be able to reach the interior of the particles. Furthermore, the lower molecular weight polymer formed when CTA is used can diffuse more easily and may allow for more rearrangement and consolidation of the domains of second stage polymer. We have conducted a series of



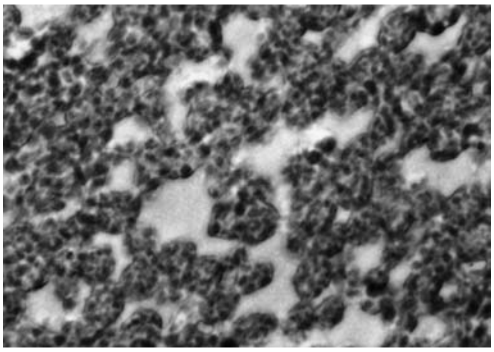
0% n-DM



0.1% n-DM



0.6% n-DM



11.25%n-DM<

experiments using a poly(methyl acrylate-co-methyl methacrylate) seed (Tg = 52C) and feeding styrene in the second stage at a reaction temperature of 70C. We used various levels of 1-dodecanethiol (n-DM) (0 to 1.25%) in solution with the styrene, producing number average molecular weights ranging from about 40,000 to 500,000. TEM images of the resulting morphologies are shown below. In the case without n-DM, an occluded core shell morphology is obtained in which polystyrene domains are formed within the particle but are preferentially located towards the outside. In the experiments with 0.25 and 0.6% n-DM, very similar morphologies are obtained indicating little effect of the CTA on morphology at these concentrations. In the experiment with 1.25% n-DM, a completely occluded morphology is obtained. The domains are now located uniformly throughout the particle and are considerably larger. This indicates that chain transfer agents do affect morphology both by allowing more penetration of the second stage radicals, as well as allowing more consolidation of the phase separated domains. However, this effect is not drastic, as significant changes were only observed at the highest CTA concentration in which the molecular weight of the second stage polymer was greatly decreased.

Radical entry in emulsion polymerization: estimation of the critical length of entry radicals via a simple lattice model

(to appear in Macromolecules, autumn 2002)

Yan Dong and Donald C. Sundberg

A lattice model has been utilized to calculate the free energy change upon oligomeric radical (derived from persulfate initiators) adsorption onto a latex particle dispersed in an aqueous phase. Variations in this free energy change with oligomer chain length allow one to predict the so-called Z-mer length at which adsorption is spontaneous. Z-mer lengths for commonly used homopolymers range from 1 to 8 (for 2-ethylhexyl acrylate and methyl acrylate, respectively). The lengths predicted for styrene and methyl

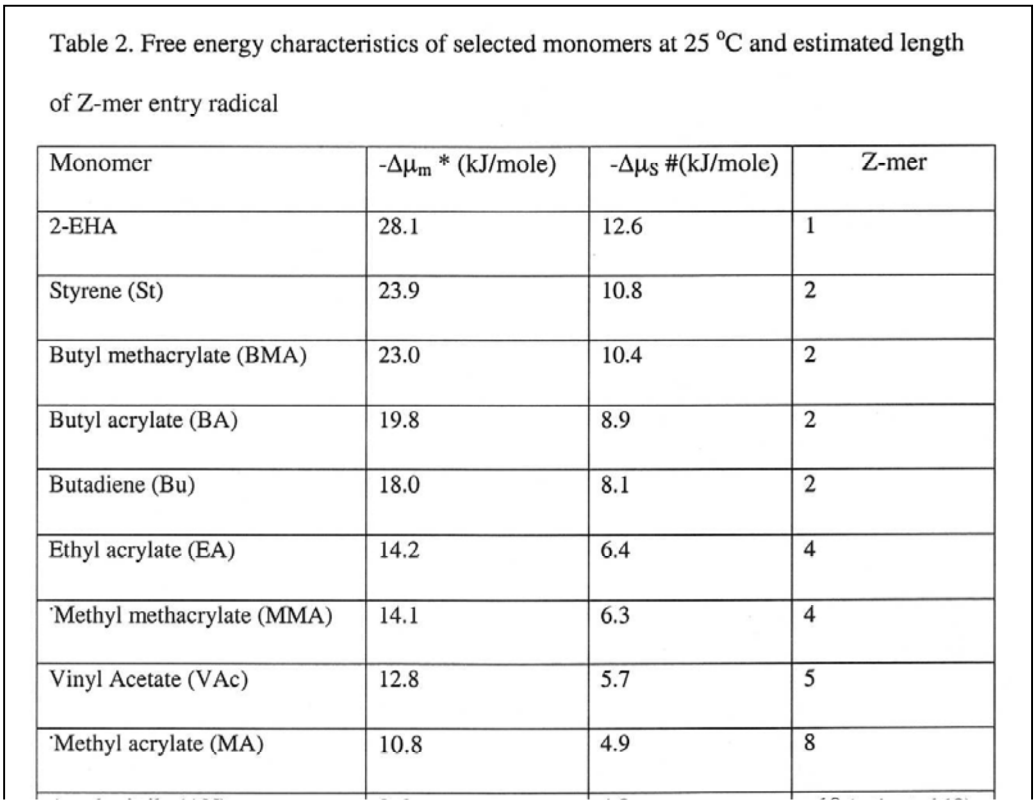


Table 2. Free energy characteristics of selected monomers at 25 °C and estimated length of Z-mer entry radical

Monomer	$-\Delta\mu_m$ * (kJ/mole)	$-\Delta\mu_S$ #(kJ/mole)	Z-mer
2-EHA	28.1	12.6	1
Styrene (St)	23.9	10.8	2
Butyl methacrylate (BMA)	23.0	10.4	2
Butyl acrylate (BA)	19.8	8.9	2
Butadiene (Bu)	18.0	8.1	2
Ethyl acrylate (EA)	14.2	6.4	4
˙Methyl methacrylate (MMA)	14.1	6.3	4
Vinyl Acetate (VAc)	12.8	5.7	5
˙Methyl acrylate (MA)	10.8	4.9	8

Figure 5

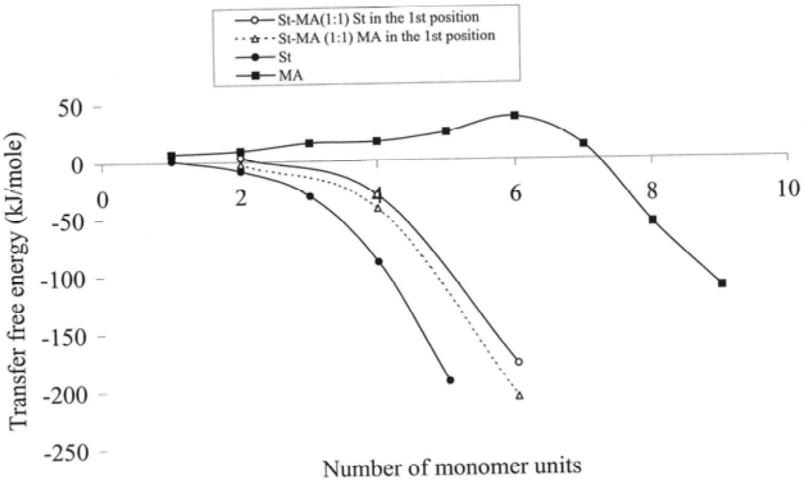


Figure 5. Changes in free energy of transferring a radical ($\Delta\mu_P$) derived from St and MA copolymerization with the total number of the monomer units in the radical. Variations due to first position placement noted for an overall composition of 50% (mole) St.

Figure 8

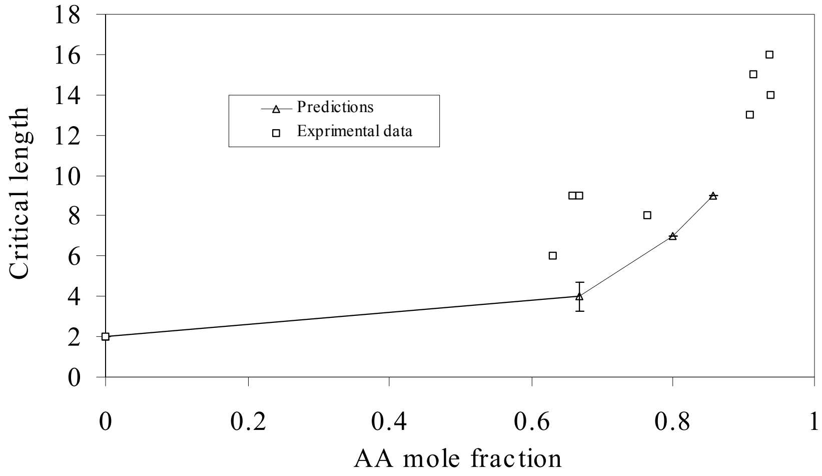


Figure 8. Changes in the average critical length of entry radicals derived from St-AA copolymerization with AA mole fraction. Error bars are the standard deviations calculated from two different 1st position placements of the two monomers

Estimation of polymer/water interfacial tensions: hydrophobic homopolymer/water interfaces

(as revised for publication in Journal of Colloid and Interfacial Sciences, 2002)

Yan Dong and Donald C. Sundberg

In this study, quantitative models for monomer/water and the corresponding polymer/water interfaces were developed. The monomer/water interface was modeled within the framework proposed by Li and Fu (1) for organic liquid/water interfaces. We took a similar approach with that which others used to simulate micelle formation of surfactants and block polymers in developing the model for the polymer/water interface. In this model, the Gibbs free energy of interfacial formation was decomposed into two components: transfer free energy of a polymer segment to the interface and mixing free energy within the interface. Interfacial tensions were then estimated using concentration gradient theory. The ratio of the number of total nearest neighbors of a site in a lattice within the interface to that located in each of the adjacent planes was found to be the important correlating factor. It was shown that this ratio for monomer/water interfaces and that for polymer/water interfaces are linearly related. The polymer in the interface is likely to be in the form of short polymer segments (2-4 monomer units) rather than dangling chain ends. The estimation of polymer/water interfacial tension from the models established in this work is in reasonable agreement with experimental observation.

Table 1. Calculated and measured monomer/water interfacial tensions ($\gamma_{M/w}$)

Monomers*	Mutual solubility(23)		δ_w-δ_M(24) (cal/cm^3)$^{1/2}$	V (cm^3/mole)	A(25) (×10^{9}cm^2/mole)	$\int_{x''_w}^{x'_w} (\Delta\bar{G}mix)^{1/2} dx$	m_M	$\gamma_{M/W}$ (mN/m)	
	x''_M	x'_w						Observed	Calculated
MA	0.0113	0.1179	12.3	50.2	7.26	0.637	0.0048	8.1	7.7
MMA	0.0027	0.0702	12.1	59.5	9.91	0.970	0.0075	12.2	12.7
BA	0.00028	0.0477	12.4	77.7	11.31	0.889	0.0132	17.5	17.9
BMA	0.00008	0.0498	12.9	85.0	13.15	0.8781	0.0166	19.2	20.2
St	0.00005	0.0040	12.0	66.3	8.27	1.373	0.0189	31.9	31.4

*MA: methyl acrylate, MMA: methyl methacrylate, BA: n-butyl acrylate, PBMA: n-butyl methacrylate, St: styrene.

Table 2. Calculated and measured polymer/water interfacial tensions ($\gamma_{P/w}$)

Polymers	δ_w-δ_P(24) (cal/cm^3)$^{1/2}$	V* cm^3/mole	$\int_1^0 (\Delta\bar{G}mix)^{1/2} dx_W$	m_P	$\gamma_{P/W}$ (mN/m)	
					Observed#	Calculated
PMA**	14.8	41.5	0.482	0.0053	---	7
PMMA	13.9	48.8	0.482	0.0397	16	16
PBA	14.2	67.0	0.482	0.0945	22	24
PBMA	14.5	73.2	0.482	0.1251	26	28
PS	14.3	57.4	0.482	0.1347	32	31

*calculated with the density of the polymers; #standard deviation: ~ ± 1 mN/m; **PMA: poly(methyl acrylate), PMMA: poly(methyl methacrylate), PBA: poly(n-butyl acrylate), PBMA: poly(n-butyl methacrylate), PS: polystyrene.

Poly(ethylene glycol) Coated Monodisperse Micron-sized Composite Polymer Particles

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ABSTRACT: Polystyrene/poly(styrene-poly(ethylene glycol) monomethacrylate) or PS/P(S-PEGMMA) composite polymer particles in the size range of one to several microns were prepared by seeded copolymerization. Monodispersed micron-sized polystyrene (PS1) particles were first prepared by dispersion polymerization, which were then used as seed particles to carry out seeded copolymerization with styrene and poly(ethylene glycol) monomethacrylate (PEGMMA). Several micron-sized polystyrene (PS2) particles were prepared from monodispersed micron-sized PS1 particles by modified activated swelling method. These PS2 particles were finally used as seed particles to carry out seeded copolymerization with styrene and PEGMMA. For comparison, some swelling experiments were also carried out in presence of macromonomer. The size distribution and particle morphology were analyzed by light and scanning electron microscope. FTIR-ATR technique was used to detect the presence of poly(ethylene glycol) or PEG unit on the surface of particles. The results indicate that seeded copolymerization in the final step is the best way to prepare several micron-sized composite polymer particles containing PEG on the surface.

Figure 3 shows the SEM photographs of unwashed CP(1000)1 (Fig. 3a) and CP(4000)1 (Fig. 3b) composite polymer particles obtained after seeded copolymerization of styrene and macromonomer with 1.65 µm-sized PS1 seed particles. Figure 3a shows that the CP(1000)1 composite polymer particles are arranged in unusually both hexagonal and cubic patterns as it is indicated by the lines in the left part of Fig. 3a. This replica also shows the region of hexagonal loose packing, which might indicate a transition to cubic arrangement. Such an arrangement is not common and observed occasionally with monodispersed particles and is referred as twin-formation.[13] In both photographs no submicron-sized (S-PEGMMA) copolymer particles were observed. This indicates that in each case seeded copolymerization proceeds smoothly that is without any secondary nucleation. The surfaces of composite polymer particles are not smooth, particularly visible at higher magnification and coagulated as some unreacted oligomers may be deposited during drying of the sample preparation for SEM. In contrast light microscopic pictures of composite polymer particles shown in Figure 4 shows stable colloidal dispersion.

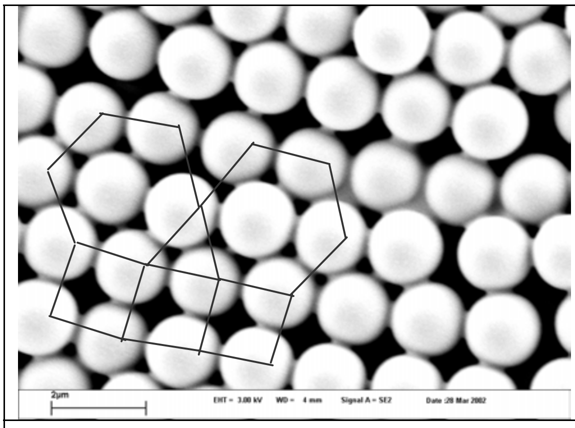	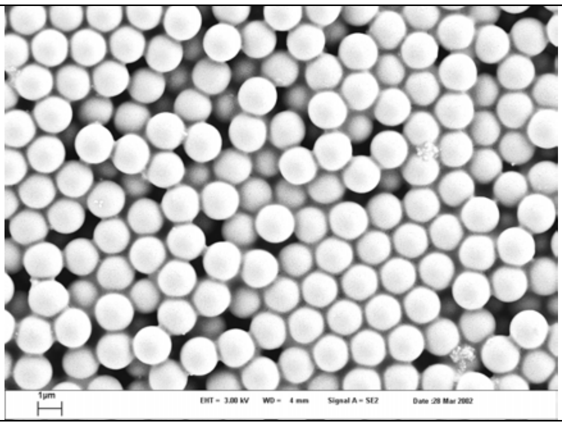
Figure 3a	Figure 3b

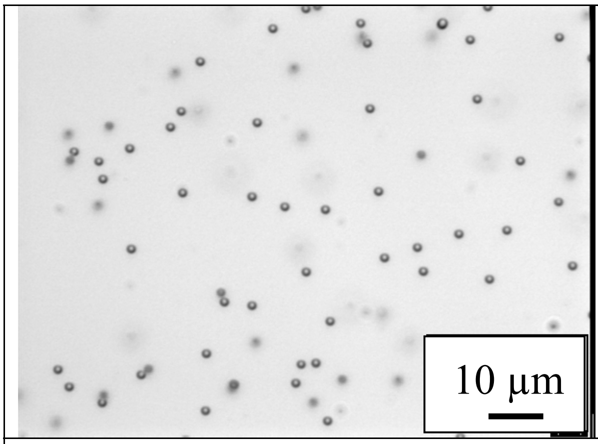	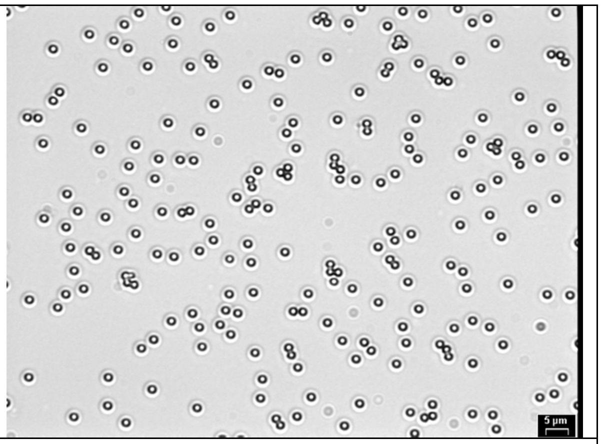
Figure 4a	Figure 4b

A New Approach towards Redispersable Polyelectrolyte-Surfactant Complex Nanoparticles

Hans-Peter Hentze*, Viktor Khrenov and Klaus Tauer
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Abstract

Redispersable and weakly cross-linked block copolymer particles with core-shell structure were prepared by the use of a macroinitiator. Subsequent sulfonation of the polystyrene core and complex formation with a variety of cationic surfactants lead to sterically stabilized, redispersable polyelectrolyte-surfactant complex particles with spherical shape and diameters of about 300 nm. Spontaneous microphase separation of the hydrophobic surfactant tails and the hydrophilic entities of the polyelectrolyte and the surfactant headgroups induce mesostructure formation within the particle cores. The characteristic lengths of the formed mesostructures depend mainly on the chain lengths of the surfactants and vary between 2-4 nm. For the first time pre-formed nanoparticles were used as constrained nanogeometries for polyelectrolyte-surfactant complex formation.

Results and Discussion

Redispersable core-shell polymer nanoparticles are obtained by free-radical emulsion polymerization. The initiating species, a poly(ethylene oxide) radical, is formed by the reaction of Ce^{4+} with poly(ethylene glycol) with a molecular weight of 20000 g/mol. The covalently bond poly(ethylene oxide) shell induces sterical stability of the polymer particles in dispersion. The hydrodynamic diameter of the freeze-dried and redispersed latex particles in water was determined as 386 nm by dynamic light scattering. Subsequently the polystyrene core was sulfonated to obtain a polyelectrolyte network structure. The purified polyelectrolyte particles were redispersed in water. Excess of cationic surfactant was added to the sulfonated particles to ensure saturation of the polyelectrolyte matrix by surfactant. This way the maximum uptake of surfactant as a function of the surfactant structure can be investigated. The chemical composition of the obtained polyelectrolyte surfactant complex particles was determined by elemental analysis. The ratio r of surfactant molecules to sulfonium groups was calculated directly from the molar ratio of nitrogen to sulfur, as all applied surfactants contain just one ammonium headgroup (Table 1).

Transmission electron micrographs of the dried polyelectrolyte surfactant complex latices show monodisperse, spherical particles with an average diameter of about 400 nm. The morphology of the original particles was retained through the whole process of functionalization and complexation. The large difference in size compared to the hydrodynamic diameter can be explained by the deswelling of the hydrophilic moieties of the complex, as well as by the collapse of the poly(ethylene oxide) shell during drying. As a consequence of the latter effect film formation takes place on the particles surfaces that causes the impression of smeared contours (Figure 3a). To investigate the inner structure of the particles ultramicrotomed samples with an average thickness of 50 nm were investigated. Micrographs of an ultramicrotomed sample (PSS-TTAB) clearly show the core-shell morphology by the difference in contrast between the collapsed poly(ethylene glycol) shell and the polyelectrolyte surfactant complex (Figure 3b).

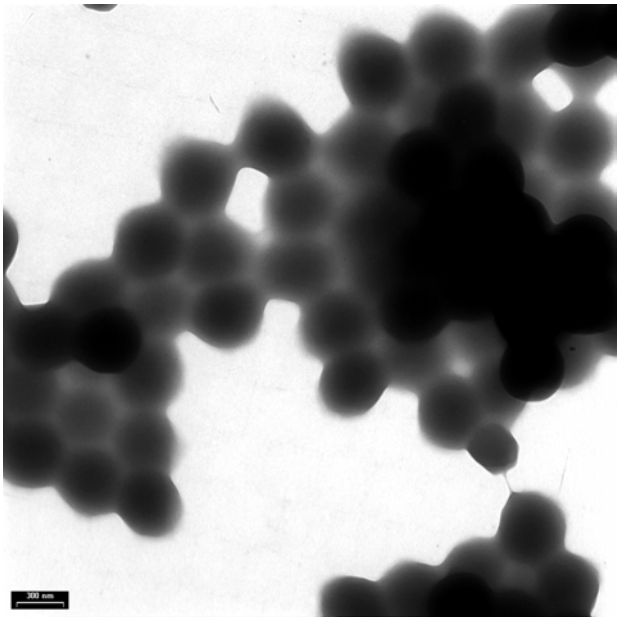

Figure 3a

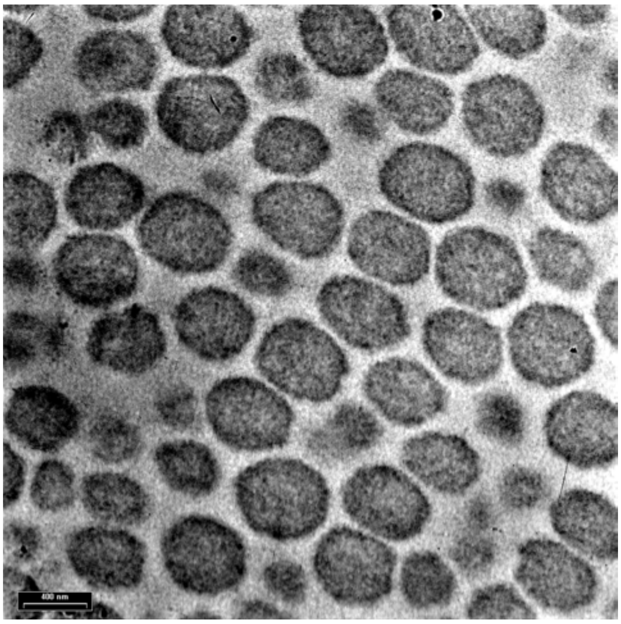

Figure 3b

The whole paper appears in Colloid and Polymer Science

Neutron Scattering of Colloidal Particle Dispersions; Contrast Variation with Homogeneous and Granular Solvents

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Abstract

The well known method of contrast variation is based on the assumption that the low--molecular solvent may be considered as a homogeneous background. The colloidal dispersion is described as a quasi- one component system. In this paper this assumption is analysed in detail. The system is described as a two-component one and use has been made of our recently derived new equation for the scattering of mixtures. It is found that when solvents are condensed liquids, this assumption is accurate when the colloid particles are not too small, say larger than $3~\mathrm{nm}$. In this limiting case the partial structure factors colloid--solvent, S_{12}, and solvent--solvent, S_{22}, are dependent on the partial structure factor of the colloid, S_{11}. When the solvent compressibility is not negligible, or when extra components -such as depletion agents- are present, deviations occur. This last situation is considered in detail for a special type of depletion agent of which the size may be comparable to that of the colloid particles. It is found that the usual contrast variation procedure cannot be applied unless the depletion agent is fully matched with the low-molecular solvent. When this is not the case the procedure must be adapted with the bonus that the (often negative) adsorption of the depletion agent by the colloid can be obtained. Two examples from the literature are given of light scattering from mixtures of colloids and polymers, where both components contribute to the scattering. This case, however, is in fact limited to low K. For higher K, SANS or SAXS experiments are needed. As a special feature it is revealed how the thermodynamics--of--mixing properties obtained from scattering can be exactly expressed in the \emph{total}-- and the \emph{osmotic} compressibilities.